

Tropospheric Ultraviolet Radiation
Assessment of Existing Data and
Effect on Ozone Formation

Systems Applications, Inc., San Rafael, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Nov 87



U.S. Department of Commerce
National Technical Information Service

NTIS

EPA/600/3-87/047
November 1987

TROPOSPHERIC ULTRAVIOLET RADIATION
Assessment of Existing Data and Effect on Ozone Formation

by

M. W. Gery
R. D. Edmond
G. Z. Whitten

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903

Interagency Agreement DW 14931805

U.S. Department of Interior
National Park Service
Denver, CO 80225

Project Officer

Bruce W. Gay, Jr.
Atmospheric Chemistry and Physics Division
Atmospheric Sciences Research Laboratory
Research Triangle Park, NC 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA/600/3-87/047	2.	3. RECIPIENT'S ACCESSION NO. PB88-130133/KS
4. TITLE AND SUBTITLE TROPOSPHERIC ULTRAVIOLET RADIATION Assessment of Existing Data and Effects on Ozone Formation	5. REPORT DATE November 1987	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M. W. Gery, R. D. Edmond, and G. Z. Whitten	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Systems Applications Inc. 101 Lucas Valley Road San Rafael, California 94903	10. PROGRAM ELEMENT NO. A101/E/75/01 - 6204 (FY-88)	11. CONTRACT/GRANT NO. IAG DW14931805
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Final (3/86 - 7/87)	14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		
16. ABSTRACT This study to determine the impacts of future changes in stratospheric ozone and surface temperature on urban air quality was carried out in two parts. The first part assesses the quality of existing ultraviolet data and approaches available for using these data to determine chemical photolysis rates. The second part involves testing the photochemical model for a number of urban data sets under conditions of decreased stratospheric ozone and increased surface temperature. The results of the study indicate an increase in ambient ozone, H ₂ O ₂ , and PAN concentration occur for most cities with decreasing ozone column. An increase in ambient temperature results in most cases with an increase in oxidants. PAN, however, which is temperature sensitive exhibits in many cases a decrease with increasing ambient temperature.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 100
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

10

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under Interagency Agreement, DW14931805. Don Henderson supervised the agreement for the National Park Service.

It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

This study was performed to determine the impact that potential changes in stratospheric ozone concentrations and surface temperatures might have on the chemical processes that create tropospheric ozone and cloud acidification precursors. The investigation consisted of two distinct parts. First, an assessment was performed of the ultraviolet radiation information and molecular absorption cross section and quantum yield data currently used in air quality simulation. This assessment addressed both the quality of existing data and approaches available for utilizing these data to determine chemical photolysis rates in the troposphere. Particular attention was paid to the photolysis reactions of ozone, formaldehyde, and acetaldehyde because these species absorb light in the spectral region where surface ultraviolet irradiance could increase due to decreased stratospheric absorption by ozone.

The algorithms and data resulting from this assessment were used in the second portion of the study to determine photolysis rates that might occur in the troposphere under future conditions of decreased stratospheric ozone. The sensitivity of photochemical dynamic processes was tested for a large number of urban airshed data sets under conditions of decreased stratospheric ozone and increased surface temperatures. The predicted surface ozone and hydrogen peroxide concentrations resulting from incremental changes in the assumed future stratospheric ozone and temperature parameters were analyzed for each city and for specific groups of cities. Instances of greater future oxidant forming potential were most common for cities with already high hydrocarbon control requirements. The increased energy input during future scenarios provided more rapid ozone formation in all cases, indicating the possible exposure of a larger portion of the urban population to higher ozone concentrations nearer to the center of the urban plume.

CONTENTS

Abstract.....	111
List of Figures.....	vi
List of Tables.....	xi
1 INTRODUCTION.....	1
2 ASSESSMENT OF ULTRAVIOLET SPECTRAL DATA AND CALCULATION OF TROPOSPHERIC PHOTOLYSIS RATES.....	5
3 SIMULATION OF URBAN PHOTOCHEMISTRY UNDER CONDITIONS OF FUTURE GLOBAL CHANGE.....	57
4 DISCUSSION OF URBAN SIMULATION RESULTS.....	122
5 CONCLUSIONS AND RECOMMENDATIONS.....	154
References.....	161
Appendix A: INPUT DATA USED FOR THE OZIPM/EKMA SIMULATION.....	165
Appendix B: PHOTOLYSIS RATE RATIOS (to j_{NO_2}) AS A FUNCTION OF ZENITH ANGLE FOR A NUMBER OF TEST CITIES.....	176

FIGURES

1-1	A simple representation of the coupling of atmospheric chemical and physical processes that could result in increased ultraviolet penetration to the troposphere.....	3
2-1	Ozone absorption cross section.....	7
2-2	Simplified representations of extraterrestrial flux and solar irradiance of 0 and 30 km above the earth's surface.....	8
2-3	Extraterrestrial flux distributions of the World Radiation Center.....	12
2-4	Extraterrestrial flux distributions of the World Radiation Center and the World Meteorological Organization.....	13
2-5	Extraterrestrial flux distributions of the World Radiation Center for the middle ultraviolet region.....	15
2-6	Extraterrestrial flux distributions of the World Radiation Center and the world Meteorological Organization for the middle ultraviolet region.....	16
2-7	Comparison of Braslau and Dave model results with Schippnick and Green calculations for similar conditions.....	19
2-8	Comparison of Braslau and Dave model results with Schippnick and Green calculations for similar conditions at different zenith angles.....	21
2-9	Surface irradiance data for zenith angles of approximately 20, 65, and 80 degrees measured at ground level in rural North Carolina.....	28

2-10	Actinic flux for 20 and 60 degree solar zenith angles in bin sizes of 1 and 5 nm.....	30
2-11	Photoaction spectra for NO ₂ using 1 and 5 nm bins.....	34
2-12	Comparison of absorption cross sections for formaldehyde.....	41
2-13	Photoaction spectra for formaldehyde to stable products and formaldehyde to radicals.....	42
2-14	Photoaction spectra for acetaldehyde using 1 and 5 nm bins.....	44
2-15	Comparison of relative j-value curve shapes with respect to solar zenith angle for the five major photolytic species.....	45
2-16	Comparison of photoaction spectra for j _{NO2} and j _{O1D} for 20 and 60 degree solar zenith angles.....	46
2-17	Comparison of 1 nm photoaction spectra for j _{HCHO_r} with spectra calculated with 10, 5, and 1 nm bins.....	48
2-18	Comparison of 1 nm photoactio spectra for j _{HCHO_s} with spectra calculated with 10, 5, and 1 nm bins.....	49
2-19	Comparison of measured and calculated j _{O1D} values.....	54
3-1	Single-day urban modeling data-set selection process protocol.....	73
3-2	Calculated zenith angles for Seattle, Washington and Los Angeles, California for 1 August.....	76
3-3	Calculated j _{O3} values for Seattle, Washington and Los Angeles, California for 1 August at 0.300 and 0.200 cm-atm overhead ozone column.....	77
3-4	Results of OZIPM future sensitivity tests for the simulation of 26 June 1974, Los Angeles, California.....	101

3-5	Results of OZIPM future sensitivity tests for the simulation of 24 June 1980, New York.....	102
3-6	Results of OZIPM future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania.....	103
3-7	Results of OZIPM future sensitivity tests for the simulation of 7 August 1980, Wahsington, DC.....	104
3-8	Results of OZIPM future sensitivity tests for the simulation of 24 June 1980, Philadelphia, Pennsylvania.....	105
3-9	Results of OZIPM future sensitivity tests for the simulation of 14 September 1984, Phoenix, Arizona.....	106
3-10	Results of OZIPM future sensitivity tests for the simulation of 1 July 1981, Tulsa, Oklahoma.....	107
3-11	Results of OZIPM future sensitivity tests for the simulation of 21 July 1980, Washington, DC.....	108
3-12	Results of OZIPM future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona.....	109
3-13	Results of OZIPM future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee.....	110
3-14	Results of OZIPM future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee.....	111
3-15	Results of OZIPM future sensitivity tests for the simulation of 31 August 1984, Phoenix, Arizona.....	112
3-16	Results of OZIPM future sensitivity tests for the simulation of 6 August 1982, Tulsa, Oklahoma.....	113
3-17	Results of OZIPM future sensitivity tests for the simulation of 11 August 1981, Seattle, Washington.....	114

3-18	Results of OZIPM future sensitivity tests for the simulation of 7 August 1981, Seattle, Washington.....	115
3-19	Results of OZIPM future sensitivity tests for the multi-day simulation of 26-27 June 1974, Los Angeles, California.....	116
3-20	Results of OZIPM future sensitivity tests for the multi-day simulation of an ozone NAAQS attainment scenario for Pheonix, Arizona.....	117
4-1	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 13 July 1979, Philadelphia, Pennsylvania.....	124
4-2	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 21 July 1980, Washington, DC.....	125
4-3	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 1 July 1981, Tulsa, Oklahoma.....	126
4-4	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 31 August 1984, Phoenix, Arizona.....	128
4-5	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 11 August 1981, Seattle, Washington.....	131
4-6	Ozone, NO ₂ , NO, and HNO ₃ plots for extreme scenarios in the future sensitivity tests--simulation of 24 June 1980, Philadelphia, Pennsylvania.....	134
4-7	Percent increase in predicted ozone over the future base case for two temperature increments and three test groups.....	137
4-8	Percent increase in predicted ozone over the future base case for two ozone column density decrements and three test groups.....	141

4-9	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--multi-day simulation of an ozone NAAQS attainment scenario for Phoenix, Arizona.....	149
4-10	Ozone, NO ₂ , H ₂ O ₂ , and PAN plots for extreme scenarios in the future sensitivity tests--multi-day simulation of 26-27 June 1974, Los Angeles, California.....	151

TABLES

2-1	Values of optical thickness for molecular and aerosol scattering, and aerosol extinction.....	24
2-2	Absorption cross sections and quantum yields for NO ₂ photolysis.....	31
2-3	Results of j _{NO2} calculations.....	33
2-4	Absorption cross sections and quantum yields for formaldehyde photolysis to radical product.....	36
2-5	Absorption cross sections and quantum yields for formaldehyde photolysis to stable products.....	37
2-6	Absorption cross sections and quantum yields for ozone photolysis to O(¹ D).....	38
2-7	Absorption cross sections and quantum yields for acetaldehyde photolysis to radical products.....	39
2-8	SAI and UNC j-value calculations for actinic flux corrected to 640 m and slightly different albedos.....	40
2-9	J-values calculated for formaldehyde photolysis at different bin sizes.....	50
2-10	Results of j-value calculations WRC extraterrestrial flux and Schipnick and Greene actinic flux formulation.....	51
3-1	OZIPM-3 listing of the CBM-X mechanism.....	60
3-2	OZIPM-3 listing of the CALL mechanism.....	65
3-3	Initial single-day data sets in the OZIPM/EKMA investigation.....	74

3-4	Design values and model results for BASE CASE simulations.....	81
3-5	Data sets used in future scenario tests.....	84
3-6	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 26 June 1974, Los Angeles, California.....	86
3-7	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 24 June 1980, New York.....	87
3-8	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania.....	88
3-9	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 7 August 1980, Washington, DC.....	89
3-10	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 24 June 1980, Philadelphia, Pennsylvania.....	90
3-11	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 14 September 1974, Phoenix, Arizona.....	91
3-12	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 1 July 1981, Tulsa, Oklahoma.....	92
3-13	Maximum hourly concentrations and percentage changes for ozone, H ₂ O ₂ , and PAN for the future sensitivity tests for the simulation of 21 July 1980, Washington, DC.....	93

3-14	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona.....	94
3-15	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 1).....	95
3-16	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 2).....	96
3-17	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 31 August 1984, Phoenix, Arizona.....	97
3-18	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 6 August 1982, Tulsa, Oklahoma.....	98
3-19	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 11 August 1981, Seattle, Washington.....	99
3-20	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 7 August 1981, Seattle, Washington.....	100
3-21	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the multi-day simulation of 26-27 June 1974, Los Angeles, California.....	118
3-22	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the multi-day simulation of attainment of the NAAQS in Phoenix, Arizona, using a modified data set from 5 July 1984.....	119

3-23	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona, with the CALL mechanism.....	120
3-24	Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania, with the CALL mechanism.....	121
4-1	Rates of increases in maximum hourly ozone concentrations with increases in temperature and decreases in overhead ozone column.....	139
4-2	"Disbenefit" to future base case maximum hourly H_2O_2 concentrations caused by increases in temperature and decreases in overhead ozone column.....	143
4-3	Comparisons of future scenario maximum hourly H_2O_2 concentrations versus original base case H_2O_2	144
4-4	Group averaged ozone responses to moderate and extreme changes to future scenario conditions.....	148

SECTION 1

INTRODUCTION

PURPOSE AND METHOD

This study was carried out to elucidate the impacts that potential future changes in stratospheric ozone concentrations and surface temperatures might have on tropospheric chemical processes resulting in formation of tropospheric ozone and cloud acidification precursors. The investigation was divided into two distinct, successive tasks. We first performed an assessment of the ultraviolet radiation information currently used in air quality simulation models for the determination of chemical photolysis rates. This assessment included both the quality of existing data and approaches available for utilizing these data to determine chemical photolysis rates in the atmosphere. The resulting algorithms and data were then used in the second task to determine photolysis rates that might occur in the troposphere under future conditions of decreased stratospheric ozone. This second task involved testing the sensitivity of chemical dynamic processes for a large number of urban data sets under conditions of decreased stratospheric ozone and increased surface temperatures.

The remainder of this section provides background information concerning the relevance of this study to current air quality issues and concerns. Section 2 describes our investigation of photolysis rate calculation methods and data, and the actinic flux algorithm, data, and results used in the second task. Sections 3 and 4 discuss the photochemical dynamic sensitivity of the data sets to potential changes to global surface temperatures and stratospheric ozone concentrations: the former describes models, mechanisms, and input data from various city-specific data sets; the latter discusses simulation results, with particular emphasis on photochemical dynamics and the impacts of various degrees of change on specific data sets. Conclusions and recommendations are presented in Section 5. Appendixes contain city-specific input data used in the sensitivity tests.

BACKGROUND

In recent years scientists have become increasingly aware that potential chemical modification of the the upper atmosphere by trace gases may produce an overall global warming by blocking the escape of thermal infrared radiation. This phenomenon is commonly referred to as the Greenhouse effect (Dickinson and Cicerone, 1986; Ramanathan et al., 1985; Wang et al., 1986). Several climatic and atmospheric modeling studies have also predicted that the chemical reactions of halocarbons (Cicerone et al., 1983; Prather et al., 1984), methane (Craig and Chou, 1982) and N_2O (Weiss, 1981) will cause future decreases in overall stratospheric ozone levels. One consequence of this decrease in stratospheric ozone levels would be an increase in the penetration of ultraviolet radiation to the troposphere, since stratospheric ozone is the principal attenuator of radiation in this spectral region. In addition to resulting in a probable increase in the incidence of skin cancer, a greater transmission of ultraviolet radiation would augment a principal energy source responsible for photochemical reactions in the troposphere. This, in turn, would cause an increase in the rates of a number of photochemical reactions critical to smog formation. The combination of possible temperature increases with an increase in ultraviolet radiant energy might alter the energy balance of the atmosphere in such a way that anthropogenic impacts on the stratosphere might again manifest in the troposphere because of stronger physical coupling between both regions (see Figure 1-1).

These potential increases in specific photochemical reaction rates, resulting from potential increases in thermal and radiant energy, have been largely ignored in studies of future chemical changes within the planetary boundary layer. Enhanced photochemical reactivity could increase the prevalence and magnitude of regional and urban ozone formation, and augment the urban contribution of acid precursors by increasing the production capacity of oxidized species. This study involved an initial analysis of the possible impacts of these changes. Because the effects of projected global changes on near-surface photochemistry will vary with the characteristics of each airshed tested, we chose to analyze a large number of different test sets. Large numbers of data sets are currently available only for urban areas whose compliance with the air quality standards for ozone must be verified. Since urban photochemical systems are the most studied, and probably the best understood, and since their precursor loading could make them the most sensitive to potential global changes, we chose to investigate global impacts on this type of system first.

In such a sensitivity study, it is also necessary to formulate some understanding of the possible ranges of projected surface temperature and stratospheric ozone changes anticipated. Our methodology was to analyze

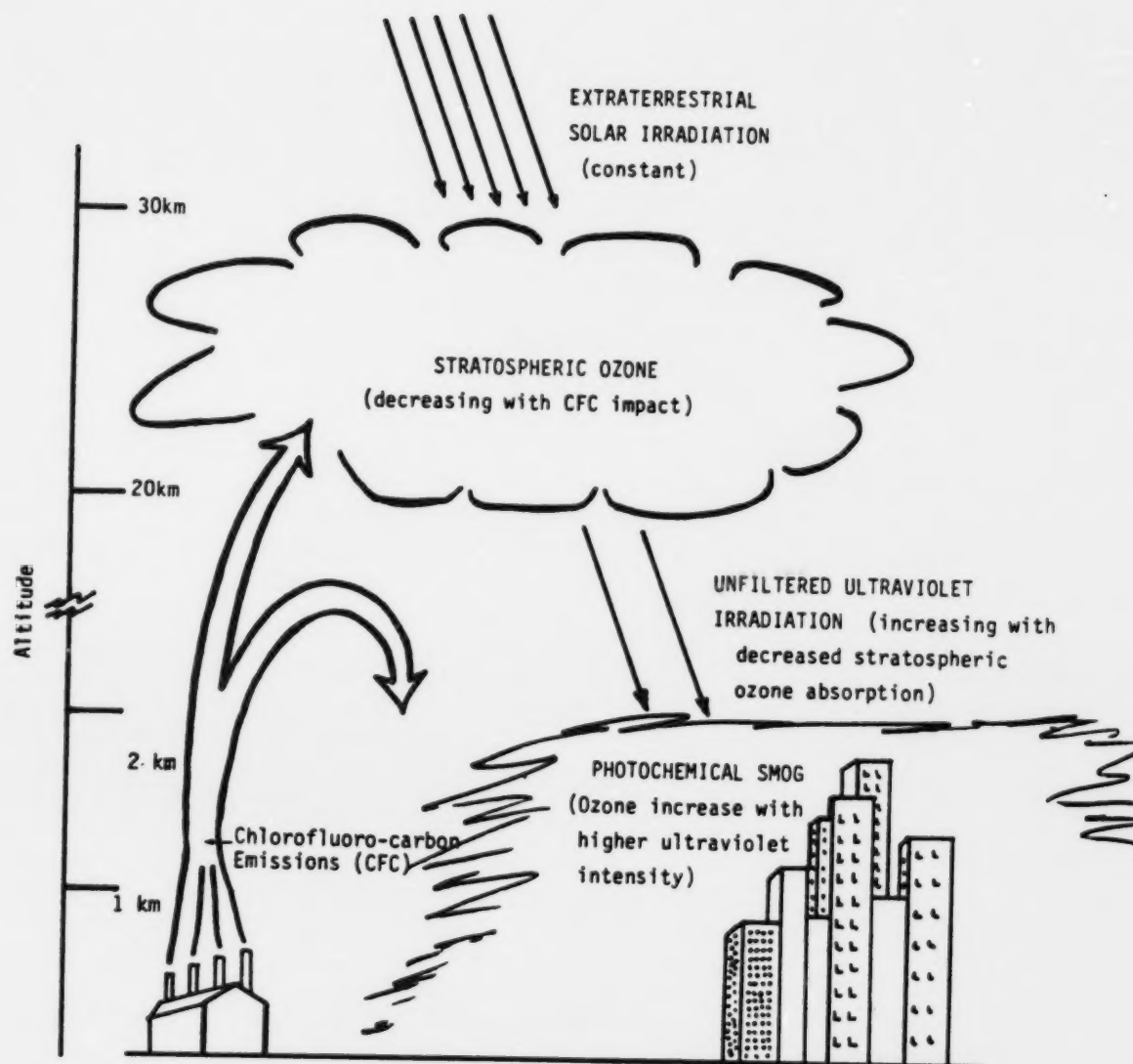


FIGURE 1-1. A simple representation of the coupling of atmospheric chemical and physical processes that could result in increased ultraviolet penetration to the troposphere.

available information, and then to devise two sets of values representing moderate and extreme future conditions. The moderate values were selected to be midway between future projections for the period 2010 to 2030, while the extreme values represented high but possible conditions, especially for later decades.

It is beyond the scope of this discussion to consider the complex perturbations that may alter future surface temperatures. However, recent efforts in global climate modeling (Dickinson and Cicerone, 1986; Wang et al., 1986; Ramanathan et al., 1985) indicate that global warming could increase the average temperature as much as 1 to 3 K by the year 2030. Therefore, in the scenarios considered in this work, we used present surface temperature data, and incremented those values by 2 and 5 K to generate future case data sets.

Because a complex set of chemical and physical dynamic processes are involved in potential future changes to mid-latitude ozone column density, projections of concentration changes into the next century are extremely uncertain. On the basis of chemical modeling of chlorocarbon and bromocarbon chemistry, Prather and coworkers (1984) projected a potential decrease in ozone column density of more than 15 percent by the middle of the next century. These projections appear to be supported by measurements of solar-backscattering ultraviolet radiation from the Nimbus 7 satellite. In recent years, decreases of about 0.5 percent/year have been measured, but comparisons between the Nimbus 7 and earth-based instruments render those numbers somewhat uncertain (Kerr, 1987). For our investigation, we chose a base-case ozone column of 0.300 cm-atm for all simulations. This represents approximately the monthly average at North American latitudes for the July and August period when most measurements in the test data sets were performed (Iqbal, 1983). Daily weather conditions specific to each data set are assumed to be contained in the simulation of each base case data set. At any rate, the perturbations caused by stratospheric ozone depletion are dominant since over 90 percent of atmospheric ozone is at upper levels. The moderate and extreme overhead ozone column conditions chosen in this study were 0.25 and 0.20 cm-atm, representing 16.7 and 33.3 percent decreases in ozone for the future test period.

SECTION 2

ASSESSMENT OF ULTRAVIOLET SPECTRAL DATA AND CALCULATION OF TROPOSPHERIC PHOTOLYSIS RATES

This section describes the processes, methods of calculation, and uncertainties associated with determination of photochemical impacts in the lower troposphere caused by depletion of stratospheric ozone.

PHYSICAL AND CHEMICAL PROCESSES AFFECTED BY FUTURE DEPLETION OF STRATOSPHERIC OZONE

The most direct way that depletion of stratospheric ozone could induce greater photochemical reactivity in the lower troposphere (and possibly cause tropospheric ozone concentrations to rise) would be through an alteration in the magnitude of radiant energy transfer processes, i.e., a physical-chemical coupling of the stratosphere and troposphere, as opposed to mixing resulting from atmospheric motion. This linkage of two generally isolated atmospheric regions (Figure 1-1) is often ignored and we briefly describe this process next.

The light that is incident on the uppermost part of the atmosphere due to radiant energy from the sun is referred to as extraterrestrial flux. The calculation of all other radiant energy values for all atmospheric conditions is derived from this extraterrestrial flux value. Although the energy output of the sun is fairly constant and well known (see Iqbal, 1983), the spectral distribution of the solar constant is less well determined. As photons penetrate the atmosphere, various processes affect the transmission of radiation to the earth's surface. The most important of these are absorption (and re-radiation) by gases, aerosol absorption and scattering, and Rayleigh (molecular) scattering. In this report, we address two types of processes that affect radiative transfer:

- (1) Alteration of the global temperature balance by increases in the concentrations of trace gases that absorb and reradiate energy at longer wavelengths.

- (2) Depletion of stratospheric ozone by some trace gases, allowing greater transmission of ultraviolet energy that would have originally been absorbed by the ozone to penetrate more deeply into the atmosphere.

The first process has been discussed in Section 1. The second is addressed in the remainder of this section.

As shown in Figure 2-1, ozone absorbs light in a number of spectral regions (Calvert and Pitts, 1966). Of particular interest are the bands of Huggins that occur between 300 to 350 nm. Because the ability of ozone to absorb light increases with decreasing wavelength, ozone in the upper atmosphere limits the transmission of ultraviolet radiation to the earth's surface. Below 300 nm, the ability of ozone to absorb radiation increases dramatically into the Hartley bands (200 to 300 nm), resulting in the cut-off of short wavelength ultraviolet transmission to the earth's surface. This cutoff is depicted as line b in Figure 2-2 (adapted from Bahe et al, 1979a). Note also that at an arbitrary point 30 km above the surface (line c), where a large percentage of the atmosphere is below the viewer, the ultraviolet cutoff is shifted to the shorter wavelengths. In addition, a "window" opens around 210 nm (area d), allowing extremely high-energy light to penetrate that region. The higher wavelength side of this "window" is defined by the falloff of ozone absorption in the Hartley bands (Figure 2-1); the lower wavelength side results from the increased absorption of molecular oxygen (which increases dramatically around 190 nm).

Although the depletion of stratospheric ozone needed to cause the degree of surface solar irradiance shown in Figure 2-2 would have to be very extreme, the figure does indicate the spectral region in which an increase in ultraviolet irradiance due to diminished stratospheric ozone absorption would occur. This increase in ultraviolet surface irradiation should be manifest in the shifting of the ultraviolet cutoff a small number of nm toward the blue end of the visible spectrum. The increase is confined to a rather small region between 310 and 280 nm because the change depends completely on the absorption characteristics of ozone, which is a much poorer absorber of radiation above 310 nm. However, though the range of the increase is small, a number of key tropospheric trace species photolyze to very reactive products only upon absorption of radiation at the edge of the ultraviolet cutoff. Therefore, even though the change in total available radiant energy may be relatively small, because of the highly localized nature of the absorption, the increase in certain tropospheric photolysis rates would be much larger.

Photolysis of stable molecules is the major source of new radicals in tropospheric gas-phase chemistry. In atmospheres capable of sustaining

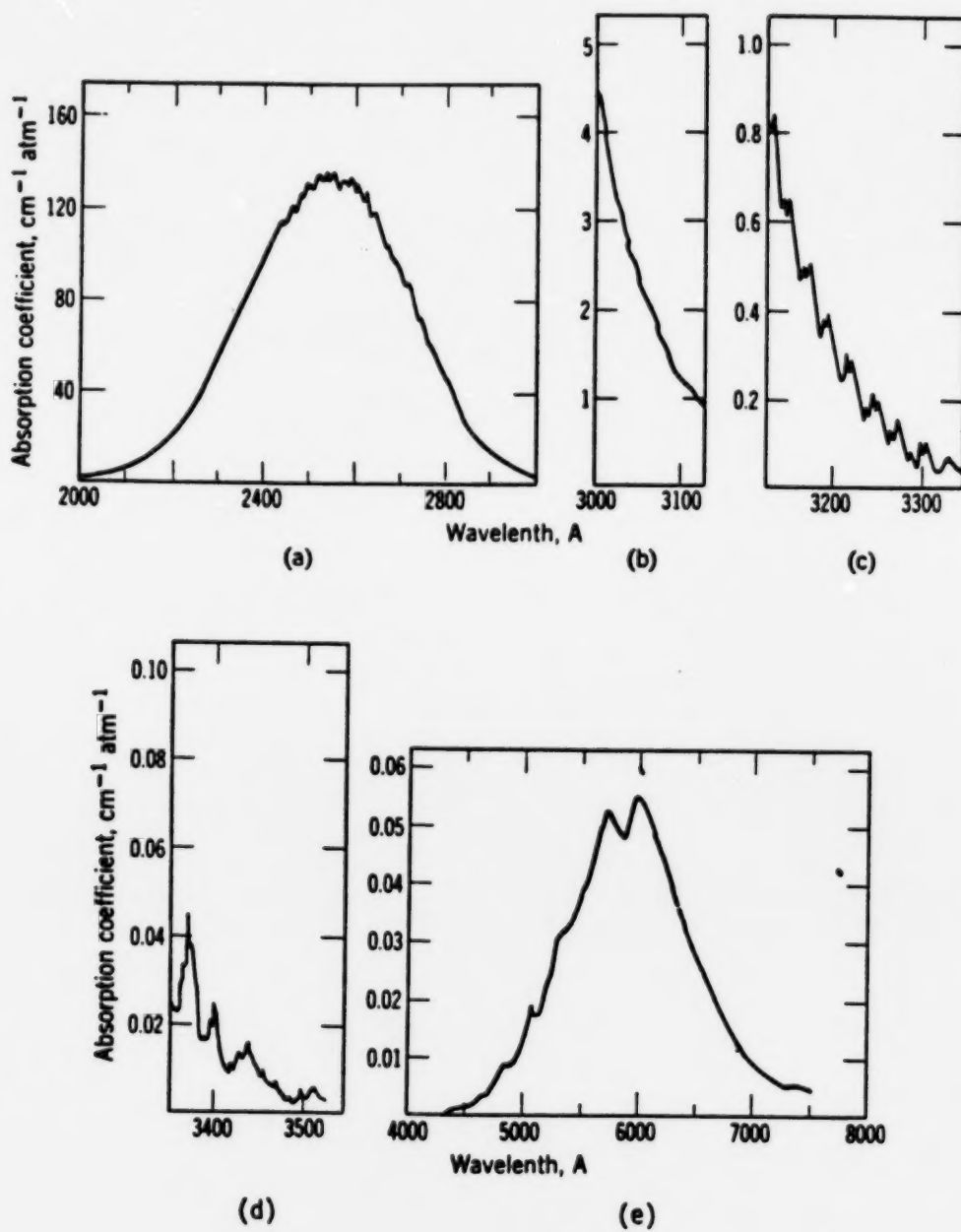


FIGURE 2-1. Ozone absorption cross section ($10\text{\AA} = 1\text{nm}$). Source: Calvert and Pitts (1966).

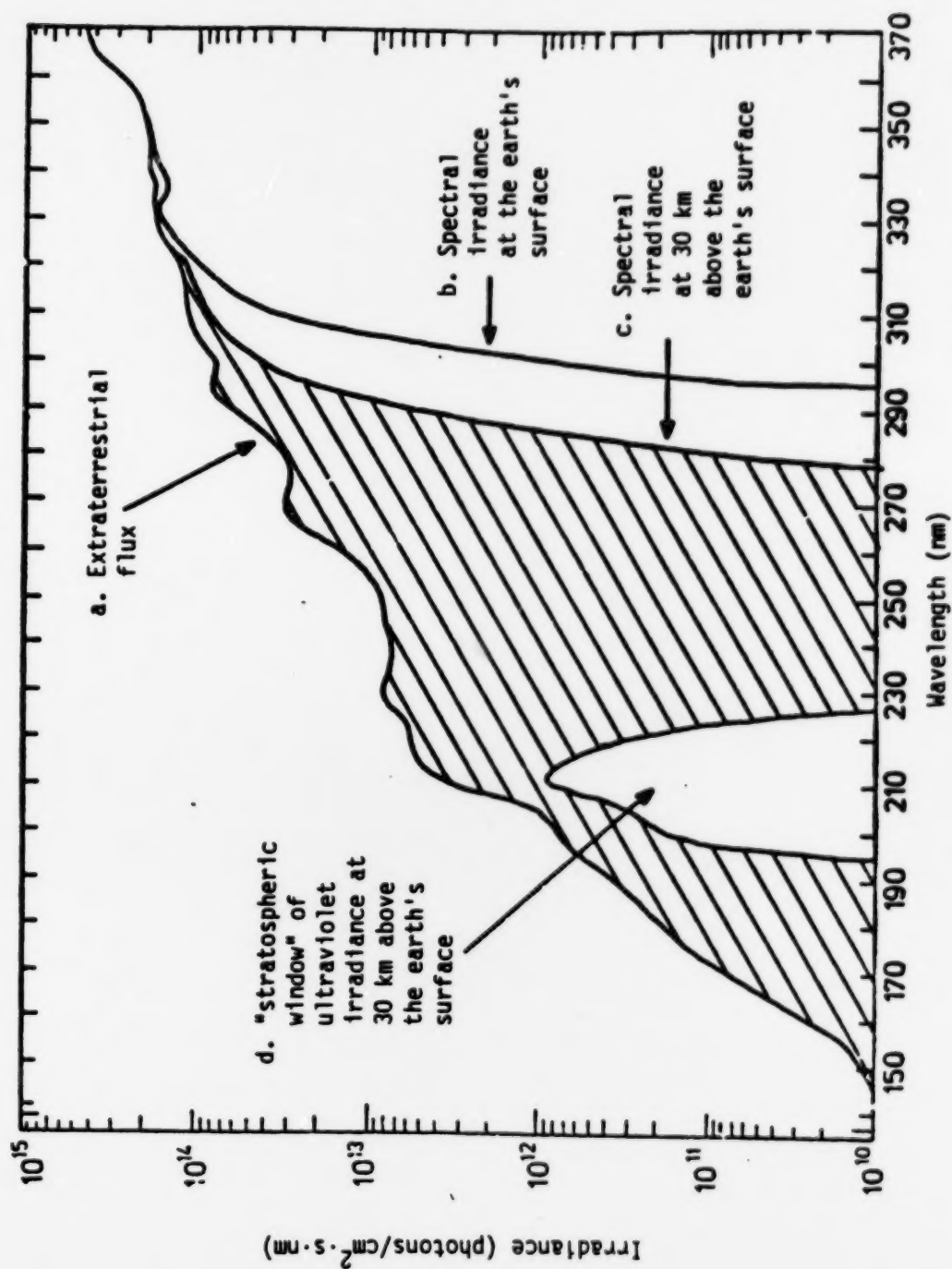
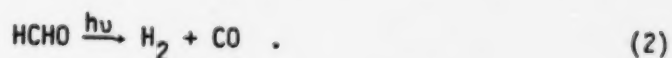
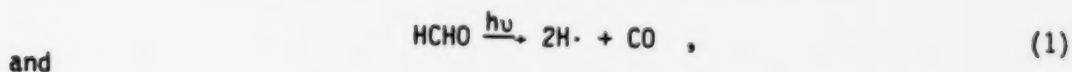


FIGURE 2-2. Simplified representations of extraterrestrial flux and solar irradiance of 0 and 30 km above the earth's surface. (Adapted from Bahe et al., 1979a).

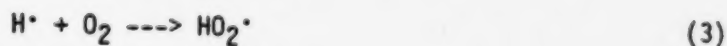
even a moderate rate of photochemical reactivity, a greater production rate for new radicals would tend to increase the initial and continued oxidation of organic compounds, resulting in additional thermochemical radical generation and sustained production of additional stable species capable of more photolysis. Therefore, the increased radical mass flux that would result from potential enhancement of some photolysis reactions could translate into more reactive tropospheric photochemistry. The result could be increased production of those oxidized species now regulated as photochemical oxidants (urban ozone), or of other compounds (peroxides) critical to the formation of acidic precipitation after transport out of an urban area.

With this in mind, it is obvious that accurate determination of key photolysis rates, especially for periods when the "radical pool" is limited (early in the day), is critical if proper representation of the radical balance is to be achieved in a photochemical kinetics model. As we discuss next, the most significantly affected tropospheric photolysis rates should be those of ozone [to produce $O(^1D)$] and aldehydes, both well-characterized pollutants generated during episodes of photochemical smog.

The formaldehyde emitted from automobiles and stationary sources is usually a product of incomplete combustion. Formaldehyde is also produced chemically in the troposphere, since it is a major oxidation product of virtually all organic molecules. The two formaldehyde photolysis reactions that could be enhanced by increased ultraviolet radiation due to depleted stratospheric ozone are



Obviously, reaction 1 is of greater concern here because it forms highly reactive radical products. In the atmosphere, $H\cdot$ reacts almost exclusively with oxygen molecules to form the hydroperoxy radical:



$HO_2\cdot$ can contribute to radical oxidation reactions in a number of significant ways, e.g.,



which not only oxidizes NO to NO₂, but also produces a hydroxyl radical that can then react with almost all organic and inorganic trace species in the troposphere. Whitten (1983) has shown that reaction 1 is often the main source of radicals responsible for the photochemical chain reactions leading to urban smog. In addition, reaction 1 is more sensitive to changes in ultraviolet radiation in the spectral region of potential increases than is reaction 2. Hence, we consider the potential effects on this process in some detail.

The tropospheric photolysis of ozone to electronically excited oxygen atoms is thought to be the second most important source of the radicals that drive smog formation:



The O(¹D) radical is extremely reactive and almost always reacts in the troposphere through one of two paths:



where M is O₂ or N₂, and



again producing hydroxyl radicals.

In reactive, oxidizing atmospheres, however, the role of ozone photolysis differs from that of formaldehyde. At low levels of oxidation potential, the excited oxygen atoms tend to accelerate smog reactions, making the atmospheric chemistry more efficient in generating ozone from minimal precursor emissions. However, at the highest or most severe ozone levels, the excess radicals can partially suppress the ozone peak, making the precursors seem less efficient in generating ozone. Hence, the chemical effects on specific photochemical systems could differ for formaldehyde and ozone since these species can occur at different times during an episode of photochemical smog and produce different photochemical impacts. In addition, because we are considering the effect of greater ultraviolet transmission to the troposphere due to a decrease stratospheric ozone, the resulting enhancement of irradiation to the surface should occur precisely at the wavelengths that are optimum for tropospheric ozone absorption. Therefore, the relative increase in photolysis rate for this process should be larger than that for formaldehyde.

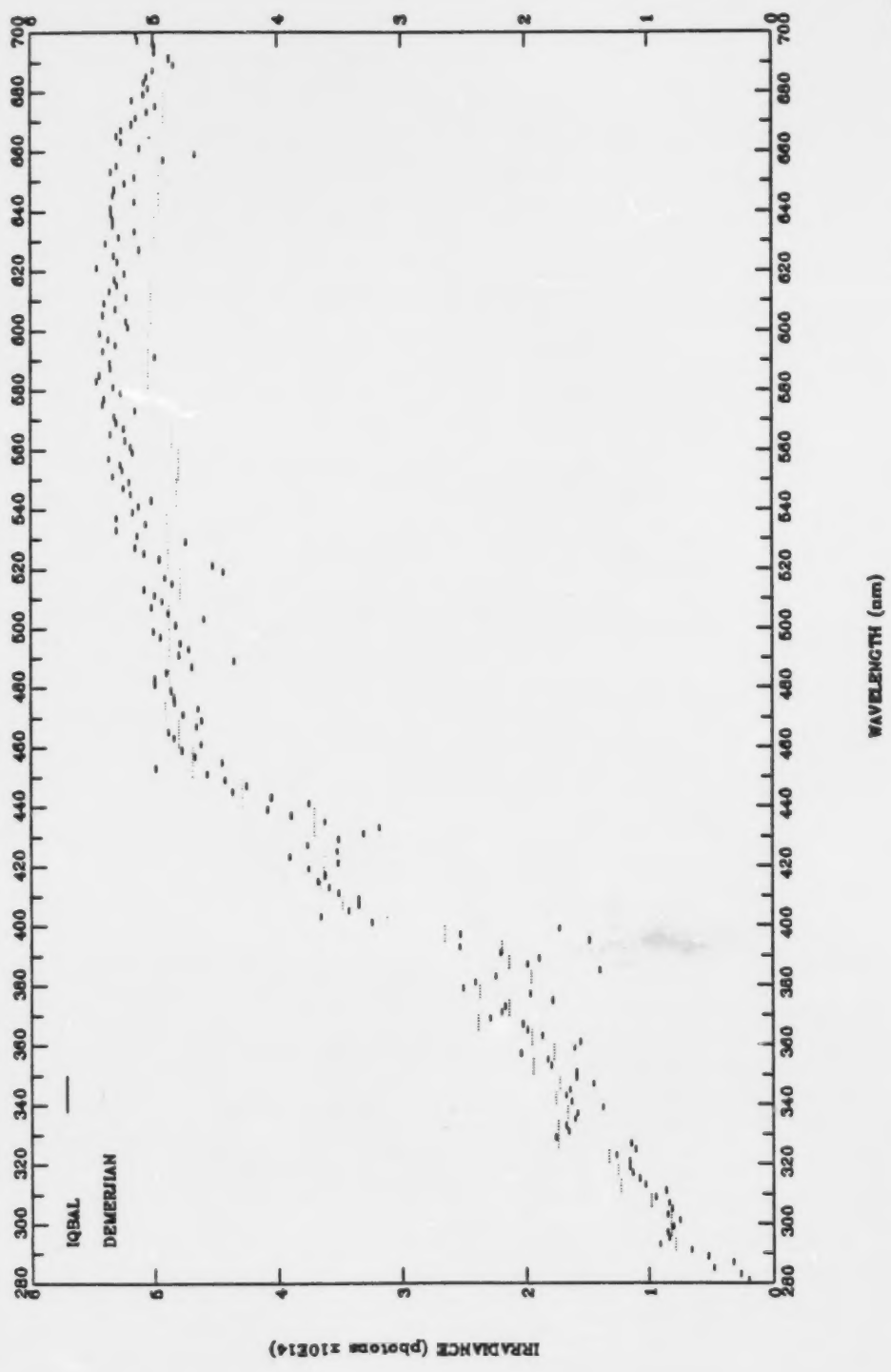
ASSESSMENT OF EXISTING DATA, RADIATION MODELS, AND UNCERTAINTIES IN THE CALCULATION OF TROPOSPHERIC PHOTOLYSIS RATES

Extraterrestrial Flux Data

Tropospheric photochemical kinetics models used to predict the chemical impact of stratospheric ozone depletion require as input a measure of the ultraviolet radiant energy in the atmosphere near the surface so that the photolysis rates of various chemical species can be determined. The relative intensity and spectral distribution of surface radiation is affected by numerous atmospheric radiative transfer processes throughout the day for each location and elevation. Because the number of measurements needed to provide such a multi-dimensional distribution of information is prohibitive, analytical characterizations of physical radiative transfer processes are utilized to determine these flux values for each set of atmospheric conditions. In all cases, an extraterrestrial flux distribution is used as the initial boundary condition or energy source.

The spectral region from about 280 nm to 800 nm is of interest in the calculation of atmospheric photolysis rates for photochemically active trace species. The values for solar irradiance, especially at the high energy end of this region, are still somewhat uncertain, though improvements have been made to the entire data set over the last decade. The solar constant distribution is compiled at the mean earth-sun distance, which occurs in April and October. During other times of the year, the extraterrestrial flux changes by as much as 3.4 percent (Demerjian et al., 1980). The work by Demerjian and coworkers is one of the most quoted sources of extraterrestrial flux used by tropospheric photochemists. They considered six sources of solar irradiance measurements and eventually utilized the then most recent values of DeLuise (1975) in the critical region of 300 nm to 400 nm, noting a disagreement of up to ten percent for specific intervals among the different data sets considered. These values are in 5 nm bins at shorter wavelengths, and 10 and 20 nm bins at longer wavelengths and are shown in Figure 2-3.

Additional information has recently become available in the form of summaries by Iqbal (1983) and the World Meteorological Organization (WMO) (1985). The principal differences between these summaries and earlier work reside in the high energy end of the spectra; rocket-borne measurements contributed to the earlier data and reexamination of instrument variation now provides a somewhat different interpretation of previous results. The recommended WMO spectrum is shown in Figure 2-4. Bin sizes are 5 nm, with the exception of slightly smaller bins near 280 nm. Both Figure 2-3 and 2-4 contain data from Iqbal (1983), which is based on work done at the World Radiation Center (WRC) by Fröhlich and Brusa (1981). These results



Reproduced from
best available copy.

FIGURE 2-3. Extraterrestrial flux distributions of the World Radiation Center (Iqbal, 1983) and Demerjian et al. (1980).

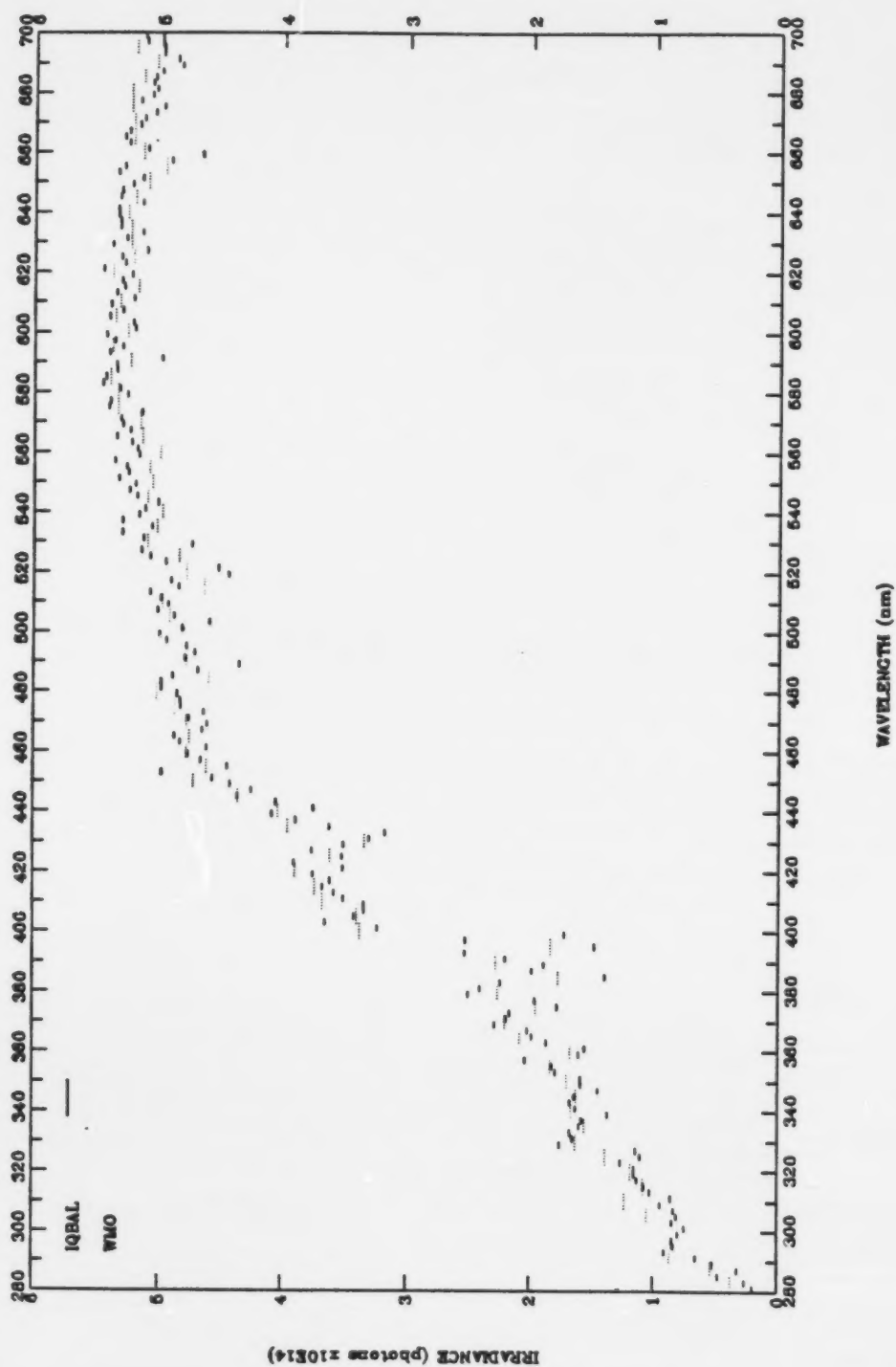


FIGURE 2-4. Extraterrestrial flux distributions of the World Radiation Center (Iqbal, 1983) and the World Meteorological Organization (1985).

are compiled into 2 nm bins; since many of the data sets used by WMO were similarly considered by the WRC, the data in Figure 2-4 agree quite closely. Comparison with the Demerjian distribution (Figure 2-3) indicates that the more recent WRC and WMO values are slightly lower for wavelengths of 300 to 400 nm, but higher for wavelengths greater than 500 nm. However, the values are generally within the stated uncertainties of about 10 percent.

For our purposes, the significant portion of the solar irradiance spectrum is the middle ultraviolet region (approximately 280 to 340 nm). There are two reasons for this: First, the ultraviolet region in which upper atmospheric ozone causes the short wavelength cutoff of surface irradiation (depicted in Figure 2-2) will be most affected by depletion of stratospheric ozone because greater transmission of short wavelength radiation to the surface will occur. Second, the photochemical result of additional radiant energy in the ultraviolet region is enhancement of the photolysis reactions that produce more photochemically reactive products, generally the radical species that contribute to the reactivity of trace gases in the troposphere.

The extraterrestrial flux data of Demerjian et al. (1980), WRC (Iqbal, 1983) and WMO (1985) are shown for the middle ultraviolet spectral region in Figures 2-5 and 2-6. The most important differences among these data occur between 300 and 330 nm. The photoaction spectra of ozone [forming $O(^1D)$] and formaldehyde (forming $2 H\cdot$ plus CO) occur in this region, with maximums for ozone between 305 and 310 nm and for formaldehyde between 310 and 325 nm. Unfortunately, comparison of the values shown in Figures 2-5 and 2-6 shows that the area between 305 and 315 nm can vary among data sets up to nearly 25 percent for specific intervals. As we discuss later, the WRC data (Iqbal, 1983) was chosen for the calculations to be used in the final simulations of our photochemical kinetics models. We felt that the inclusion of more recent measurements would provide a more complete basis than would be provided by the earlier summary of Demerjian and co-workers (1980). In addition, since the correspondence between the WRC and WMO data was usually good, we selected the WRC data for our calculations because it was available at a higher resolution. However, we will also utilize the Demerjian extraterrestrial flux data in a number of subsequent calculations because comparisons with previous calculations using those data will be useful. Both sets of data have been interpolated with a cubic spline routine to yield 1 nm bins, preserving the original bin energies in all cases.

Radiative Transfer Models and Actinic Flux Calculations

While irradiance generally refers to the flux (e.g., extraterrestrial) that is incident on a flat, horizontal surface, actinic flux refers to the

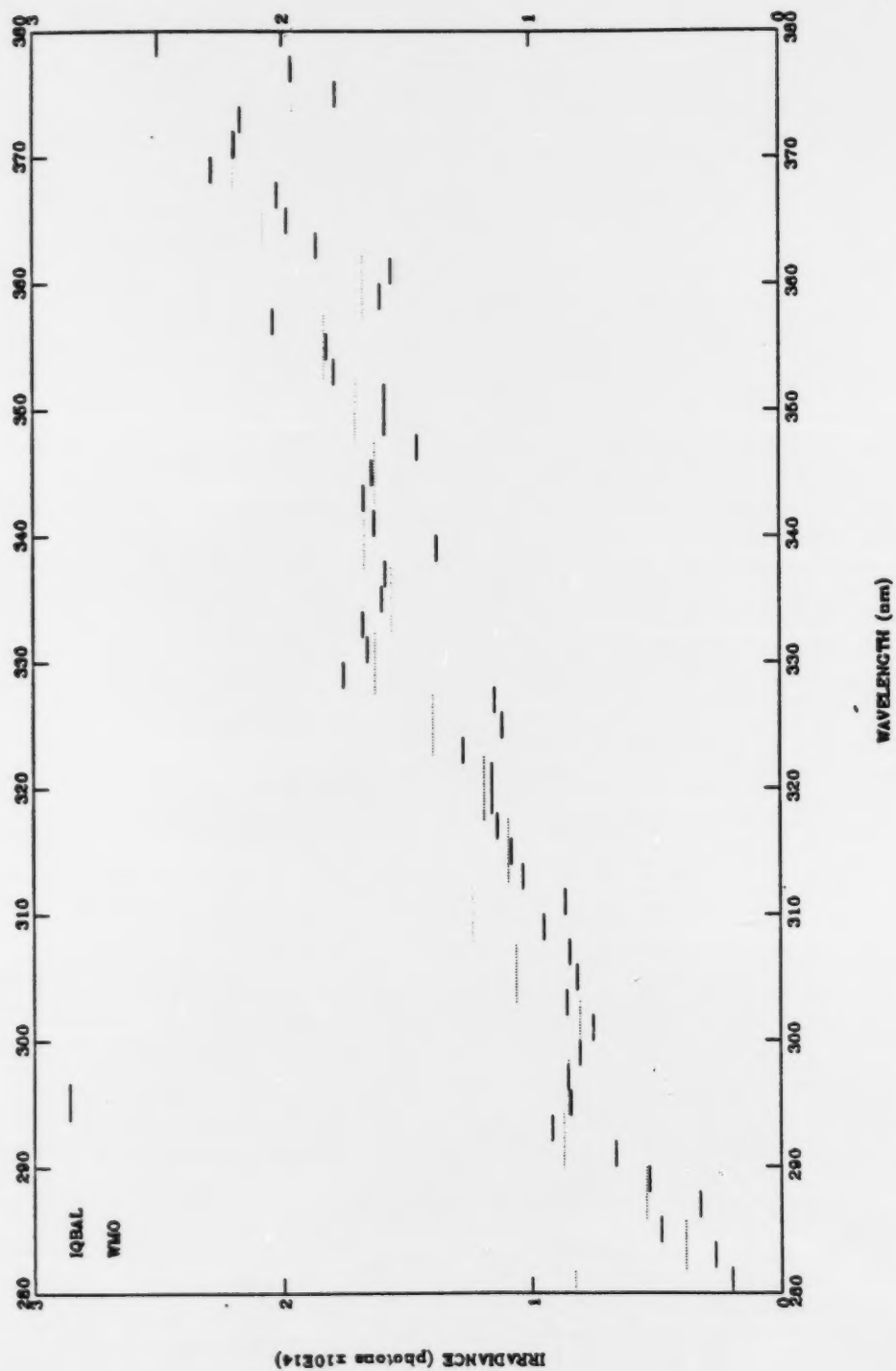


FIGURE 2-5. Extraterrestrial flux distributions of the World Radiation Center (Iqbal, 1983) and Demerjian et al. (1980) for the middle ultraviolet region.

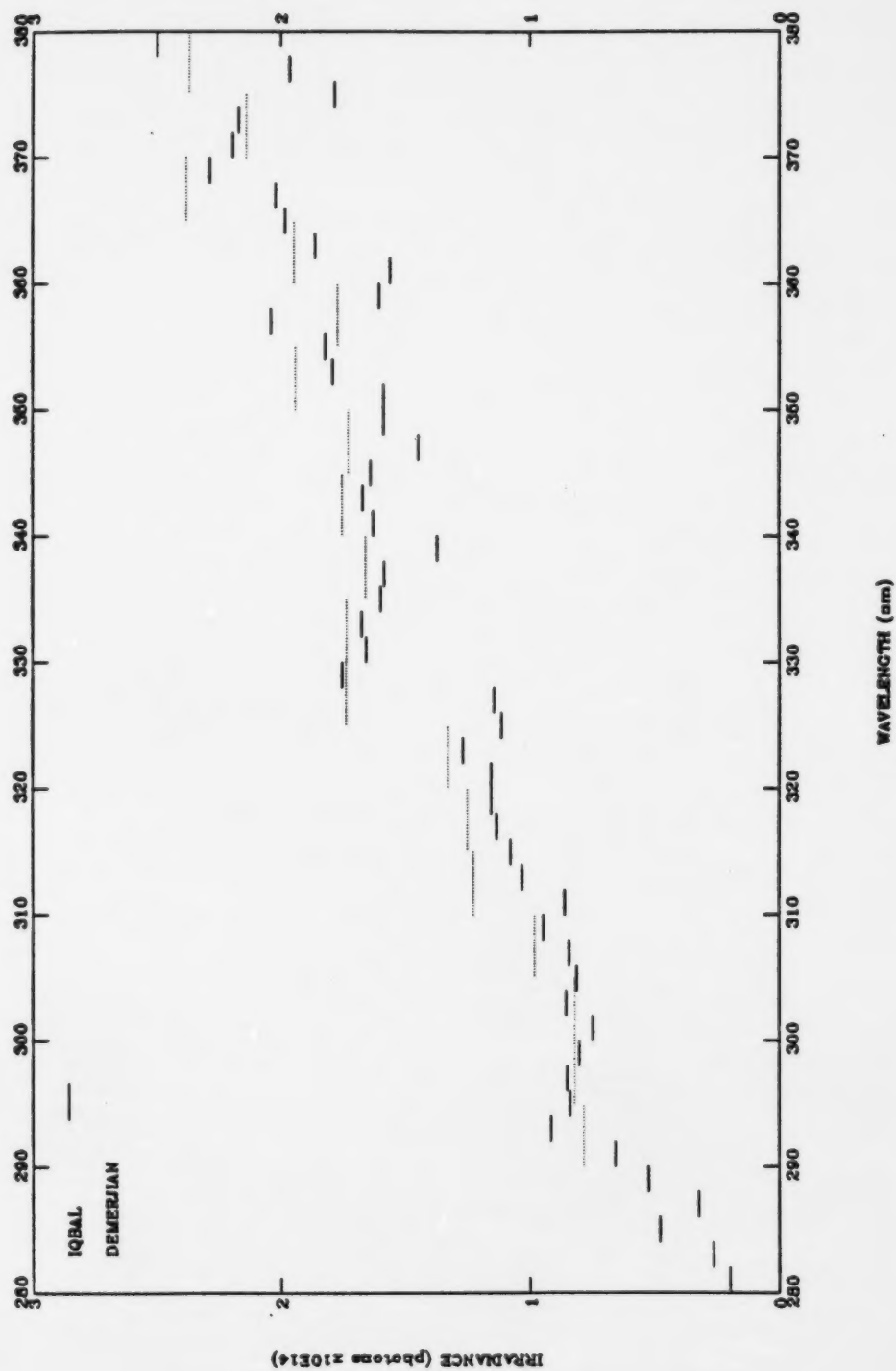


FIGURE 2-6. Extraterrestrial flux distributions of the World Radiation Center (Iqbal, 1983) and the World Meteorological Organization (1985) for the middle ultraviolet region.

flux incident on a spherical surface. This is the "correct" flux for the calculation of photolysis rates in the atmosphere because radiation, which induces the photolysis of a molecule, can come from any direction. Radiative transfer models determine the amount of direct (at the angle of the solar disc) and diffuse (incident at various other angles due to scattering, reflection, and emission) radiation, and combine these data to calculate actinic flux at various locations and conditions in the atmosphere. As noted, the initial energy source of these calculations is the extraterrestrial flux.

The most complex radiative transfer model to date was developed by Dave (1972). The complete model and six simulations are described by Braslau and Dave (1973a and b). The original version of this model was capable of addressing ozone absorption, molecular scattering, and aerosol absorption and scattering, and was later modified to include oxygen, water vapor, and carbon dioxide absorption. The atmosphere was divided into 160 layers and contained an arbitrary set of ozone and aerosol distributions. Calculations, particularly the aerosol optical calculations, were extremely time-consuming but resulted in spectrally integrated flux values stated to be accurate to within 0.5 percent. Subsequent uses of this complex model have followed two paths: Peterson (1977) and Demerjian et al. (1980) used a version of the model with 40 layers to calculate actinic flux values at various altitudes from the earth's surface for different atmospheric conditions and solar elevations. Adopting a different approach, Green et al. (1980) and Schipnick and Green (1982) used the model results as a basis for development of a simpler analytical characterization for middle ultraviolet sky light.

Both approaches have yielded information and methods useful in the calculation of photolysis rates in the troposphere. The results of Demerjian et al. (1980) and Peterson (1977), however, are in the form of tabulated actinic fluxes for a fixed ozone column density (0.295 cm-atm), but a variable aerosol distribution and surface albedo. Therefore, though these results provide very useful actinic flux conditions for simulating average, present-day ozone column scenarios, investigation of the effects of future ozone depletion requires similar calculations at different ozone column densities. Such calculations have not yet been performed. Also, better and more highly resolved measurements of extraterrestrial flux and absorption cross sections and quantum yields have now become available. Hence, new calculations would be extremely useful in future work because they could be done at a somewhat higher resolution than the earlier work and would have the credibility associated with calculations performed directly by the Dave model (as opposed to the analytical characterizations to be discussed next).

Characterization of upward and downward diffuse spectral irradiance by Green et al. (1980) and Schippnick and Green (1982) allows calculation of actinic flux in the middle ultraviolet region for a number of conditions that are necessarily variable in the study of future stratospheric ozone and climate change. However, it is limited because it is a characterization of the results of a rigorous model and not of the model itself. Therefore, the range over which it is well characterized cannot exceed the range of the original model results without some loss of certainty. Fortunately, the formulation was not a mere curve-fitting exercise, but directly accounted for the effects of physical processes, as in the model of Braslau and Dave. This approach increases confidence in its application outside the range of the Braslau and Dave results since the descriptions of the processes, as well as the results, are actually characterized.

The Schippnick and Green (1982) formulation allows calculation of downward diffuse, direct, and upward diffuse radiation. These fluxes can be determined at variable wavelengths (280 to 380 nm), solar zenith angles (0 to 86 degrees), altitudes (0 to 5 km), and albedos. The calculations depend on vertically resolved distributions of ozone and aerosol to determine optical depths for ozone absorption, molecular scattering, and aerosol absorption and scattering. An excellent technical explanation of the empirical fitting parameter is found in the works of Green et al. (1980) and Schippnick and Green (1982); we refer the reader to those publications for further detail.

A key difference among the future scenarios investigated in this study is the magnitude of the increase in actinic flux resulting from depletion of stratospheric ozone. Because the Schippnick and Green model (1982) can rapidly perform a large set of calculations, we chose it for the calculation of tropospheric actinic flux in our future scenarios of different ozone column values. We were convinced that their formulation could account for perturbations in the spectral actinic flux due to changes in the ozone column in a rigorous manner, but we wanted assurance that the absolute values of actinic flux did not deviate from the Braslau and Dave predictions for the conditions under which these comparisons were possible. Unfortunately, not all comparisons can be this complete since the Braslau and Dave model calculations were performed many years ago at bin sizes larger than those currently used. However, we have obtained unpublished, altitude-dependent flux output from the Braslau and Dave model (Schiere, 1986) as run by Peterson (1977) and Demerjian and coworkers (1980; 40 layers) to facilitate such comparisons. Figure 2-7 compares these flux values with those predicted by the Schippnick and Green formulation for four different solar zenith angles (0, 20 50 and 78 degrees) over the middle ultraviolet range using the standard input conditions of

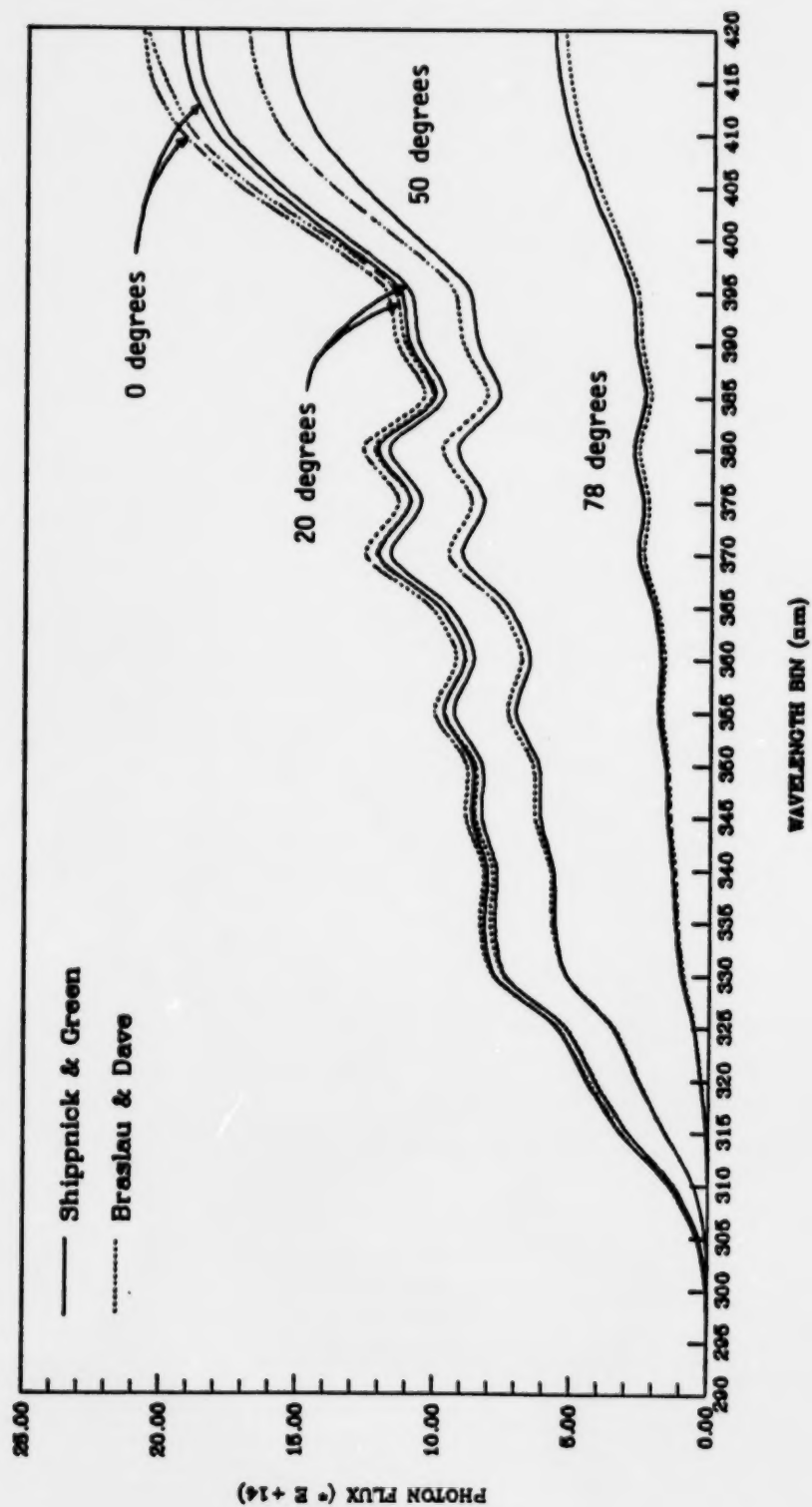


FIGURE 2-7. Comparison of Braslau and Dave model results with Schippnick and Green calculations for similar conditions.

Demerjian et al. (1980), an ozone column density of 0.295 cm-atm, and an albedo of 0.05. The analytical formulation duplicates the Braslau and Dave values for the short wavelength end of the spectrum; however, a difference exists above approximately 330 nm.

Because the Schippnick and Green formulation is designed to operate only within the spectral region bounded by 280 and 380 nm, its upper limit occurs below the long wavelength end of the NO_2 photoaction spectrum (approximately 410 nm). Therefore, even if the Schippnick and Green formulation had fit the Braslau and Dave results at the upper end of the middle ultraviolet range, calculation of some photolysis rates, such as J_{NO_2} , would not be possible. However, at the lower wavelengths the formulation appears to be quite accurate in predicting absolute actinic flux (Figure 2-8). Fortunately, this region is precisely where the effect of stratospheric ozone depletion is expected to be prominent (Figure 2-2). We therefore utilized the Schippnick and Green formulation to calculate the variations in short wavelength actinic flux resulting from a changing ozone column. However, since many other species (including NO_2 , H_2O_2 , NO_3 and HONO) have photoaction spectra too far into the red range for their calculated j -values to be affected by the localized change in ultraviolet flux due to stratospheric ozone depletion, we used the original Braslau and Dave model as formulated by Peterson (1977) and Demerjian et al.

(1980), and recently evaluated by Jeffries and Sexton (1987) to determine absolute photolysis rates of these species. The Schippnick and Green formulation could be used to determine relative changes in the longer wavelength absorbers due to ozone column variation, but it is known in advance of these calculations that the relative variation for even the most sensitive species is no more than approximately 2 percent. *

We noted earlier the dearth of actinic flux measurements at known conditions and the resulting lack of data for verification of these actinic flux formulations. Nonetheless, other types of data in the form of direct measurements of specific photolysis rates are available and can be used to test our calculations. In fact, these data provide the ultimate comparison, since they are measurements of precisely the values we are attempting to calculate. We utilize these data to evaluate our radiation and photolysis rate calculations in a following section. First, however, we briefly discuss the additional parameters and uncertainties associated with the actinic flux models, followed by consideration of the method and uncertainties involved in the calculation of specific photolysis rates from these models.

Data Requirements and Uncertainties

We have already described the available extraterrestrial flux data and the associated uncertainty. However, these models also require information

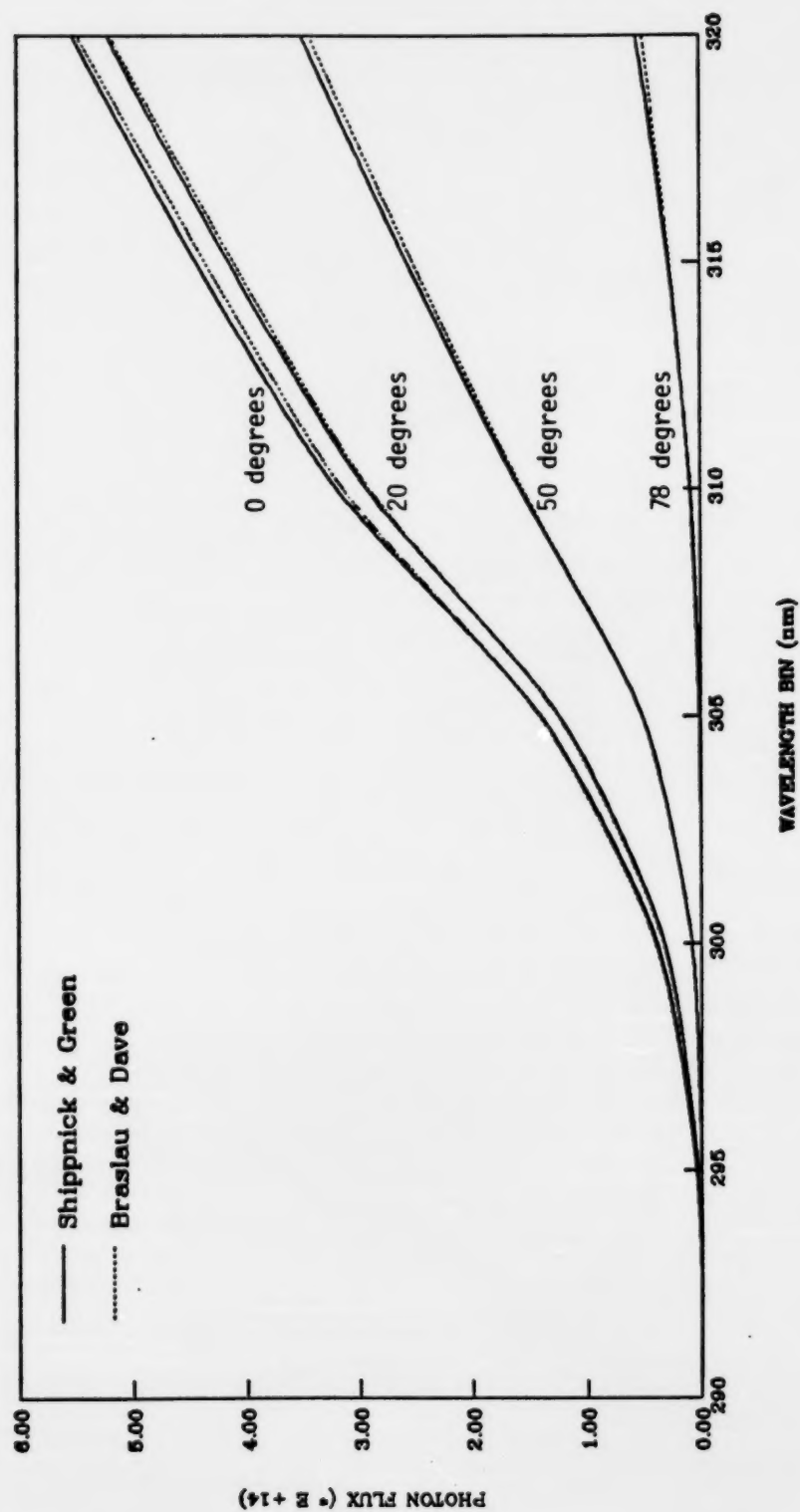


FIGURE 2-8. Comparison of Braslau and Dave model results with Shipnick and Green calculations for similar conditions at different zenith angles.

describing processes affecting radiation transfer at different altitudes of the atmosphere and at the earth's surface. In addition to our main variable, the ozone column density, consideration must be given to surface albedo, aerosol distribution, Rayleigh (molecular) scattering, and even cloud cover. Obviously, we could not vary all of these parameters during the present study. In addition, though these variables have been shown to affect calculated j-values, we have no reason to assume that there will be significant changes between present and future cases. Therefore, we briefly discuss the variables and their effects, and provide the values we utilized in subsequent calculations.

Surface Albedo

The albedo can be simply defined as the fraction of incident radiation that is reflected from a surface. This definition includes the effects of aerosol and gas molecules between the viewer and the ground. Therefore, if one looks down from a location well above the ground, most of the reflected radiation is actually from the gas and aerosol below the view-point and only partly from the generally low reflection from the ground below (Jeffries and Sexton, 1987). This is generally referred to as the regional albedo. It should not be confused with local albedo, which is calculated inches or feet above a surface. The difference in measurement points may explain discrepancies between the large values determined from satellite observations and generally smaller surface values. In their calculations of spectral actinic flux, Demerjian et al. (1980) used a "best estimate" surface albedo of 0.05 (290 to 400 nm), 0.06 (400 to 450 nm), 0.08 (450 to 500 nm), 0.10 (500 to 550 nm) and 0.11 (550 to 660 nm). Their work showed that slight variations in albedo could provide small differences in actinic flux calculations, since their calculations indicate about a 2 percent increase in actinic flux for a 1 percent increase in albedo through the short wavelength region. We used a value of 0.05 and a larger integrated average of 0.08 for the entire region when comparing our results with those of Jeffries and Sexton (1987). However, local albedo is extremely variable and dependent on land use. We used location-specific, monthly average ground albedo (Iqbal, 1983) during the modeling portion of this study to better define this parameter.

Aerosol Distribution

Perhaps the most difficult variables to describe are the aerosol distribution and resulting scattering and absorption optical thicknesses. The diurnal and location-specific variations in atmospheric aerosol properties are difficult to establish and are certainly poorly described by use of

only one average. Nevertheless, because such data are sparse we are forced to assume a standard distribution. However, some constraints limit the uncertainty in our application. First, the simulations performed in this study are primarily of cities that have air pollution problems and can thus be expected to have elevated aerosol loading due to anthropogenic impacts. To address this condition in our calculations, we chose optical thickness functions more typical of urban environments. In addition, because certain optical thickness functions have already been developed to describe different types of aerosol conditions for similar models [first by Braslau and Dave (1973), and later by Demerjian et al. (1980) and Schippnick and Green (1982)], we felt that these established data should be used when possible in our present work. Therefore, we used aerosol optical depths for Los Angeles, but from an area to the west of the haziest sections of the city (Demerjian et al, 1980). Data for both aerosol scattering and extinction are shown in Table 2-1.

Molecular Scattering

Also shown in Table 2-1 are spectral data for molecular (Rayleigh)-scattering normal optical thickness. These values were used by Demerjian et al. (1980) and Green et al. (1980), and were originally derived from Penn-dorf (1957). The treatment of sky cover in this and other models is difficult because the phenomenon is not easily or completely described. There are no provisions for inclusion of this variable in actinic flux or most photochemical kinetics simulation models. In application, the least sky cover, or the minimal attenuation of solar irradiance, is generally associated with high rates of ozone formation that occur on the episode days that we investigated. Therefore, we assumed clear-sky conditions in all simulations.

Altitude

Both Peterson (1977) and Demerjian et al. (1980) addressed the issue of altitude in their calculations using the modified (40-layer) model of Braslau and Dave (1973a and b). Schere (1986) provided copies of these results in 10 nm bins for 10 zenith angles and 10 altitude levels from 0 to 4210 m above sea level. It is clear from these data that an accurate assesment of the observation point is necessary to provide an accurate basis for actinic flux calculations. Our calculations are to be utilized in a two-cell model with the top of the lower cell defined by the mixing height. We assume an average afternoon mixing height of 1280 m above the surface. Therefore, our actinic flux (and j-value) calculations were performed for an altitude 640 m above the local surface. Hence, slightly

TABLE 2-1. Values of Optical Thickness for Molecular and Aerosol Scattering, and Aerosol Extinction. Source: Demerjian et al. (1980)

Wavelength Interval (nm)	Scattering		Aerosol Extinction
	Molecular	Aerosol	
280-285	1.590	0.201	0.236
285-290	1.470	0.202	0.237
290-295	1.361	0.203	0.238
295-300	1.265	0.204	0.239
300-305	1.178	0.205	0.239
305-310	1.098	0.206	0.240
310-315	1.025	0.206	0.240
315-320	0.958	0.207	0.241
320-325	0.896	0.209	0.242
325-330	0.839	0.210	0.242
330-335	0.788	0.211	0.243
335-340	0.739	0.211	0.243
340-345	0.694	0.212	0.244
345-350	0.653	0.213	0.244
350-355	0.617	0.214	0.245
355-360	0.582	0.215	0.245
360-365	0.548	0.216	0.246
365-370	0.517	0.217	0.247
370-375	0.489	0.217	0.247
375-380	0.462	0.218	0.248
380-385	0.438	0.219	0.248
385-390	0.415	0.219	0.248
390-395	0.393	0.220	0.249
395-400	0.373	0.221	0.249

different j -values were determined for each city, depending on the local elevation and other factors such as local albedo. These values are discussed in a subsequent section.

Ozone Column Density

The absorption of solar irradiance by atmospheric ozone is the main variable in this study. Ozone column density is defined as the thickness of a layer that would result if all ozone directly between the surface and the top of the atmosphere were compressed to 1 atmosphere pressure at 273 K. In North America, a typical summer value is 0.300 cm-atm. These data are also given in Dobson Units (DU), which are milli-cm-atm. Therefore, the same typical value would be 300 DU. The effect of atmospheric ozone absorption is described by Beer's Law,

$$I/I_0 = e^{-[\sigma(O_3) \times \tau(O_3)/\cos(\theta)]} \quad , \quad (8)$$

where I/I_0 is the fraction of irradiance reaching the observer, $\sigma(O_3)$ is the ozone absorption coefficient (described next), and $\tau(O_3)/\cos(\theta)$ is the "effective" ozone column density. The effective ozone column density approximates the actual mass of ozone that sunlight passes through by increasing the overhead ozone column ($\tau(O_3)$) by a factor of $1/\cos(\theta)$ to account for the zenith angle (θ) of the sun. We will demonstrate that this measure of effective ozone column density can be used to unify various measurements of irradiance or actinometry performed in different locations, as long as the overhead column and zenith angle are known. We describe this process in greater detail and present our ozone absorption cross-section data in a subsequent section.

CALCULATION OF PHOTOLYSIS RATES

We have shown that the Schipnick and Green (1982) characterization provides a method of calculating actinic flux that adequately represents calculations of the more rigorous Braslau and Dave model. However, we must also demonstrate that these results, regardless of which model they come from, can be used to accurately predict atmospheric measurements. As we have noted, the principal variable input for our photochemical kinetics model scenarios will be the spectral actinic flux. Unfortunately, there are very few direct measurements of spectral actinic flux at different altitudes or locations. Often, only the downward-looking fraction is measured and little information relative to local and regional albedo, aerosol optical depths, or even ozone column density is given. Such measurements are only now becoming available at the resolution necessary to characterize the conditional dependencies of actinic flux and calculate

local photolysis rates. Collection of this type of data should be encouraged since it will provide the basic information needed to directly verify and improve the calculations of large models (Braslau and Dave) and analytical characterizations (Schippnick and Greene).

The process of chemical actinometry is a direct measurement of the effects of actinic flux. In such an experiment the photolysis rate of a chemical species (photolyzing through a specific channel) is determined by direct measurement of changes in concentrations of the initial reactant or of products formed through photolysis. For our purposes, such measurements (given accurate characterization of the measurement environment) are extremely useful since our ultimate goal is to be able to calculate these j -values for varying ozone column conditions. Therefore, where possible, we have compared these measured j -values with our calculated photolysis rates. The calculated rates are based on the actinic flux predicted for the specific conditions at the time of the actinometry experiment. As background to a comparison of our results with measured j -values, we briefly discuss calculation methods and associated data uncertainties.

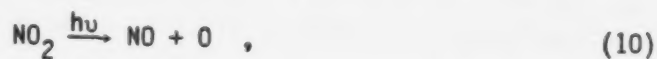
Calculation of J-values and Associated Uncertainties

The photolysis rate (j -value) of a specific molecular process is defined at any given time by the integral of the triple product, $I\sigma\phi$, over the wavelength interval of interest,

$$j_n = \int_{\lambda_{\min}}^{\lambda_{\max}} I(\lambda)\sigma(\lambda)\phi(\lambda)d\lambda \quad , \quad (9)$$

where I is the actinic flux, σ is the molecular absorption cross section and ϕ is the quantum yield for a specific photolysis process (n). From this simple formulation, it is apparent that uncertainties in j -value calculations result from two sources: (1) the measure of spectral actinic flux and its variation with time and conditions, and (2) the uncertainties associated with the experimental determination of the absorption cross section and quantum yields. The irradiance calculations have been discussed; we now concern ourselves with the remaining uncertainties inherent in the j -value calculations.

In the application of most photochemical kinetics models to the troposphere, the rate of NO_2 photolysis (j_{NO_2}),



is used as an indicator of the amount of light energy available at the time of day and conditions simulated. However, NO_2 absorbs light and photolyzes at longer wavelengths compared to the photoreceptors (ozone and aldehydes) considered significant in this investigation. It is well known that the spectral distribution of surface actinic flux changes with solar elevation; therefore, the photolysis rates of the species that absorb primarily at shorter wavelengths will not linearly follow the j_{NO_2} value. The reason for this is apparent from Figure 2-9, which shows surface measurements of spectral irradiance in North Carolina (Jeffries, 1986) for zenith angles of approximately 80, 65 and 20 degrees. Two points can be made from these plots. First, the magnitude of these three traces increases by more than a factor of 10 between each curve as spectra from zenith angle decrease. Second, at larger zenith angles and increasing atmospheric optical thickness, the effect of increased ozone absorption (compare with Figure 2-1) is seen in the selective depletion of radiation at the ultraviolet cutoff (below 300 nm) and the Bands of Chappuis (centered at 600 nm). Therefore, though the j_{NO_2} value can be used to track the relative amount of energy available for photolysis throughout the day, a second function representing the changing spectral distribution is also included so that the absolute amount of energy available to species that absorb in other spectral regions can be determined. For this function, we use the zenith angle of the solar disk as a variable indicator. In practical applications of this method, nonlinear sets of ratios are multiplied by the experimental j_{NO_2} value for a given time of day to determine the absolute j -values of other species at that time of day and zenith angle.

In this study, we are also interested in the effect of decreased stratospheric ozone (increased ultraviolet actinic flux) on the j -values that depend on shorter wavelength radiation. Thus, another variable is introduced, that of ozone column density. Consideration of this variable results in a set of zenith-angle-dependent j -values for each different column density. Fortunately, as discussed earlier, the region of radiation change is confined to a small interval in the middle ultraviolet range (Figure 2-2), causing changes to only the j -values based on short wavelength ultraviolet radiation. The j_{NO_2} value, for instance, is very similar for all ozone columns considered in this study.

The following discussion addresses uncertainties associated with the calculation of j -values to assess the associated error in j -value determinations. We first investigate uncertainties in conditions used in our present-day base-case scenarios (0.295 and 0.300 cm-atm ozone column density) using the results of a recent evaluation by Jeffries and Sexton (1987) to provide a set of independent calculations for comparison. We have intentionally attempted to use the identical actinic flux data of Jeffries and Sexton [who used values from Peterson (1977)] to focus our investigation

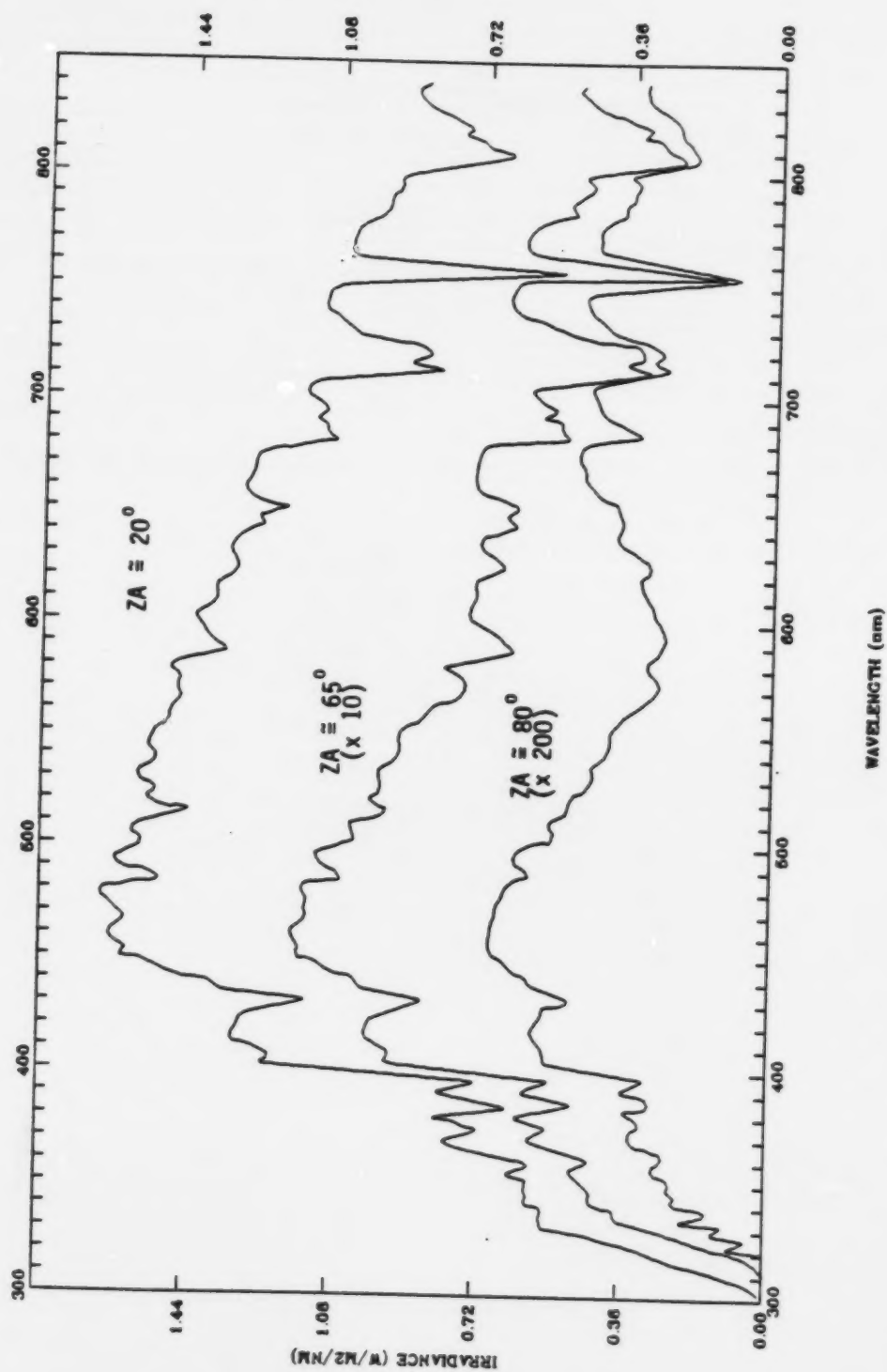


FIGURE 2-9. Surface irradiance data for zenith angles of approximately 20, 65, and 80 degrees measured at ground level in rural North Carolina. (Source: Jeffries, 1986).

on the remaining quantum yield and absorption cross-section variables. Later in this section, we briefly investigate the effect of bin size on calculations, and provide our best estimate of present-day and future j-values based on results obtained with the WRC (Iqbal, 1983) extraterrestrial flux data, the Schippnick and Greene (1982) actinic flux formulation, and varying ozone column conditions.

Specific j-values are usually calculated using a standard set of actinic flux distributions for a range of zenith angles. In this comparison, both sets of calculations use the clear-sky, ground-level actinic flux values calculated by Peterson (1977), with altitude corrections to 640 m as prescribed by Demerjian, Schere, and Peterson (1980). In most of their calculations, Jeffries and Sexton (1987) instituted an albedo correction, resulting in an integral albedo of 0.08. We use the aerosol distribution, surface albedo (0.05), and ozone column density (0.295 cm-atm) of Demerjian and coworkers (1980). Therefore, the values of actinic flux and the resulting j-values will vary slightly between investigations because Jeffries and Sexton usually corrected to an integral albedo of 0.08 and performed their numerical integration of j-values with 5 and 10 nm bins. It has been our practice to use either 1 or 2 nm bin sizes in all j-value calculations. Later in this section we present results using the WRC extraterrestrial flux data (Iqbal, 1983), which are available in 2 nm bin sizes. To utilize the actinic flux of Demerjian and coworkers (1980), we have interpolated the 5 and 10 nm bins to 1 nm values, verifying at all times that the sum of the energy within five 1 nm bins is equal to the energy in the original 5 nm bin. The spectral distributions at two zenith angles (20 and 60 degrees) for 1 nm and 5 nm bins are shown in Figure 2-10.

NO₂ photolysis rates were calculated using the absorption cross sections and quantum yields listed in Table 2-2. In this case (only), Jeffries and Sexton present calculations for a surface actinic flux data set with an albedo of 0.05, the value of our calculations. A comparison of results is given in Table 2-3*.

* Jeffries and Sexton values are designated UNC for University of North Carolina.

Actinic Flux for 20 and 60 Degree ZAs

(Source: Demerjian et al., 1980)

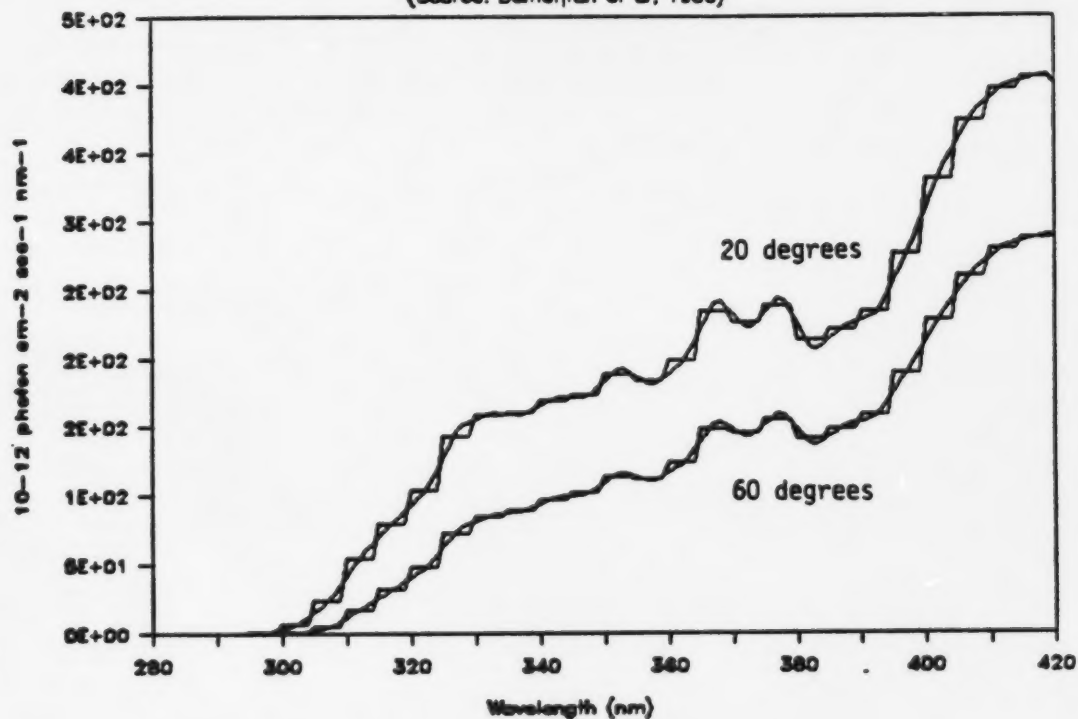


FIGURE 2-10. Actinic flux for 20 and 60 degree solar zenith angles in bin sizes of 1 and 5 nm. Areas under curves are equal. (Source: Demerjian et al., 1980).

Table 2-2. Absorption cross sections and quantum yields for NO₂ photolysis:

$$\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O} \quad .$$

Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	5.54	0.984	315	22.50	0.968
281	5.58	0.984	316	21.31	0.967
282	5.36	0.984	317	23.29	0.966
283	5.36	0.984	318	24.81	0.966
284	6.25	0.984	319	23.14	0.965
285	6.99	0.984	320	25.37	0.964
286	7.29	0.984	321	26.53	0.963
287	7.37	0.984	322	26.49	0.962
288	7.66	0.984	323	27.68	0.962
289	7.89	0.984	324	26.75	0.961
290	8.18	0.984	325	27.86	0.960
291	9.90	0.984	326	28.79	0.959
292	9.37	0.984	327	29.09	0.958
293	9.75	0.984	328	30.77	0.958
294	9.48	0.984	329	29.98	0.957
295	9.68	0.984	330	29.87	0.956
296	9.30	0.983	331	30.50	0.955
297	12.17	0.982	332	30.05	0.954
298	11.72	0.982	333	37.27	0.954
299	12.57	0.981	334	29.80	0.953
300	11.72	0.980	335	34.52	0.952
301	12.28	0.980	336	35.08	0.951
302	13.87	0.978	337	34.63	0.950
303	15.92	0.978	338	34.78	0.950
304	15.96	0.977	339	39.88	0.949
305	16.56	0.976	340	38.80	0.948
306	15.81	0.975	341	41.66	0.947
307	16.33	0.974	342	38.32	0.946
308	16.18	0.973	343	35.45	0.946
309	18.38	0.973	344	40.21	0.945
310	17.56	0.972	345	40.70	0.944
311	18.78	0.971	346	42.93	0.943
312	19.61	0.970	347	42.78	0.942
313	20.35	0.970	348	48.21	0.942
314	19.42	0.969	349	46.12	0.941

(Continued)

Table 2-2 (Concluded)



Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
350	40.99	0.940	385	59.41	0.770
351	45.20	0.939	386	53.20	0.840
352	44.38	0.938	387	56.02	0.750
353	39.88	0.938	388	59.78	0.810
354	50.40	0.937	389	60.23	0.780
355	51.30	0.936	390	60.01	0.800
356	46.05	0.935	391	58.29	0.880
357	55.80	0.934	392	60.49	0.840
358	50.37	0.934	393	54.54	0.900
359	45.53	0.933	394	55.42	0.900
360	45.13	0.932	395	58.89	0.840
361	53.87	0.931	396	61.45	0.830
362	50.40	0.930	397	56.65	0.820
363	51.23	0.930	398	64.06	0.770
364	48.74	0.929	399	56.03	0.780
365	57.81	0.928	400	67.59	0.680
366	53.98	0.912	401	65.25	0.650
367	51.86	0.896	402	57.10	0.620
368	53.42	0.881	403	51.04	0.570
369	51.82	0.865	404	60.67	0.420
370	54.20	0.849	405	63.17	0.320
371	52.12	0.833	406	53.90	0.330
372	59.81	0.817	407	47.28	0.250
373	55.02	0.802	408	62.61	0.200
374	52.12	0.786	409	59.00	0.190
375	53.53	0.770	410	57.73	0.150
376	62.35	0.780	411	58.78	0.100
377	56.69	0.920	412	53.65	0.090
378	51.74	0.820	413	70.04	0.080
379	54.68	0.870	414	59.41	0.080
380	59.86	0.900	415	60.41	0.070
381	56.62	0.810	416	48.47	0.060
382	56.36	0.700	417	53.12	0.050
383	53.72	0.680	418	55.17	0.040
384	59.67	0.700	419	52.79	0.030
			420	57.72	0.020

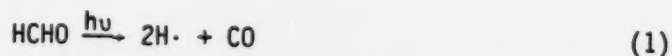
TABLE 2-3. Results of j_{NO_2} Calculations (min^{-1}).

Zenith Angle (deg)	Albedo = 0.05	
	SAI	UNC
0	0.485	0.503
10	0.481	0.499
20	0.469	0.487
30	0.448	0.464
40	0.415	0.430
50	0.366	0.379
60	0.295	0.306
70	0.194	0.202
78	0.095	0.099
86	0.020	0.019

Our results are 2 to 4 percent lower than those of UNC. In both cases, the data were taken from the NASA (DeMore, 1985) review; however, the UNC calculations are based on 5 nm bin averages of quantum yield and cross section, whereas our calculations were performed at 1 nm. The resulting photoaction spectra (the product, $I_0\phi$, versus wavelength) are shown in Figure 2-11 for a 20° zenith angle. Our calculations using 1 nm and 5 nm bins show that the variation in methodologies causes these minor j_{NO_2} differences. Such differences in j_{NO_2} are not significant and are certainly bounded by the uncertainty of the experimental quantum yield and absorption cross-section data. On the other hand, this variation does indicate that some error due to lack of resolution can develop, even for a rather wide and relatively featureless photoaction spectrum such as that of NO_2 . As we will see later in this section, uncertainties associated with bin size can grow if conditions are less favorable.

Because the photoaction spectra for formaldehyde, acetaldehyde, and ozone [to $\text{O}(^1\text{D})$] occur at short wavelengths, where the actinic flux can be enhanced by decreases in stratospheric ozone, we focus on the following four processes:

j_{HCHO} :



Photoaction Spectra for NO₂

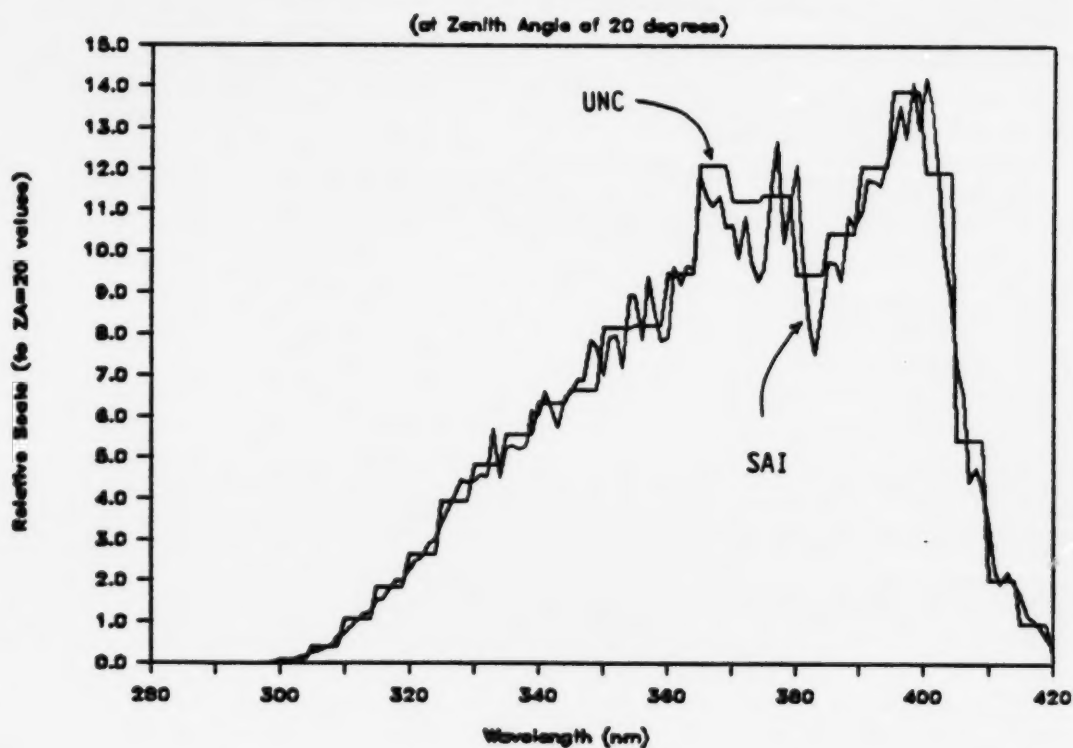
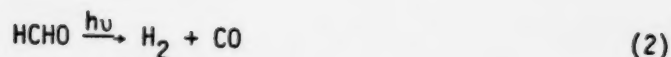
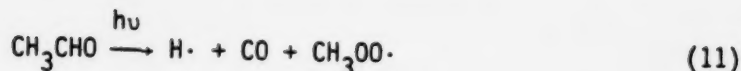


FIGURE 2-11. Photoaction spectra for NO₂ using 1 and 5 nm bins.

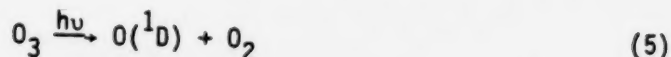
J_{HCHO_s} :



J_{ALD_2r} :



$J_{\text{O}_3\text{D}}$:

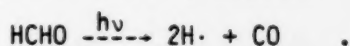


The absorption cross sections and quantum yields used for formaldehyde, acetaldehyde (ALD2), and ozone are presented in Tables 2-4 through 2-7. The absolute, zenith-angle-dependent photolysis rates (calculated as above) and the UNC values (calculated with $A=0.08$) are compared in Table 2-8 for Peterson's (1977) actinic flux corrected to 640 m (Demerjian et al., 1980).

A comparison of the formaldehyde photolysis rates given in Table 2-8 with those determined by UNC indicates the degree of uncertainty in many of the published absorption cross-section and quantum yield data (and also points out the need for atmospheric chemical actinometry and smog chamber modeling to verify the chosen rates). Calculations indicate that our J_{HCHO_r} and J_{HCHO_s} rates are approximately 85 and 65 percent of the UNC-determined values, and that a significant portion of these differences is due to the choice of quantum yield and absorption cross-section data. Our quantum yield data for both formaldehyde photolysis channels are 1 nm values that were fit by Calvert (1980) using his data and that of Moortgat and co-workers (1978, 1979). Ten nm averages of these data are approximately 0 to 10 percent lower than the 10 nm values used by UNC.

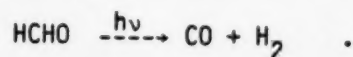
Our two major sources of absorption cross-section data for formaldehyde are Bass (1980) and Moortgat (1986). We have communicated with these researchers and obtained their data. As shown in Figure 2-12, their results differ by more than 30 percent, especially at the longer wavelength region. After considering both data sets, we used the 0.05 nm resolved data of Bass to derive 1 nm bin averages. UNC utilized 10 nm bin values given by NASA (DeMore, 1985), which were determined by averaging the two sets of absorption cross-section data. Figure 2-13 shows the photoaction spectra for both formaldehyde photolysis channels using our 1 nm values, the UNC 10 nm bins, and a 5 nm light source (the amount of light was equal for both photoaction spectra). The differences in j -values noted above result almost completely from the differences in

Table 2-4. Absorption cross sections and quantum yields for formaldehyde photolysis to radical products:



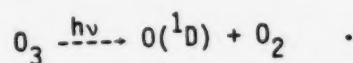
Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	2.34	0.560	310	1.03	0.760
281	1.65	0.580	311	0.81	0.750
282	0.76	0.600	312	1.49	0.740
283	0.46	0.620	313	1.55	0.730
284	3.93	0.630	314	3.99	0.720
285	3.46	0.650	315	2.88	0.700
286	2.32	0.670	316	2.79	0.690
287	0.95	0.680	317	3.59	0.670
288	2.32	0.700	318	1.65	0.650
289	2.50	0.710	319	0.73	0.630
290	1.43	0.720	320	1.71	0.610
291	1.32	0.730	321	1.32	0.590
292	0.66	0.750	322	0.43	0.570
293	5.22	0.760	323	0.60	0.540
294	4.30	0.760	324	0.75	0.510
295	3.21	0.770	325	2.19	0.490
296	1.59	0.780	326	3.44	0.460
297	1.96	0.790	327	1.75	0.430
298	3.66	0.790	328	1.01	0.390
299	1.55	0.790	329	3.03	0.360
300	0.72	0.800	330	1.96	0.330
301	1.51	0.800	331	0.79	0.290
302	0.74	0.800	332	0.32	0.250
303	4.35	0.800	333	0.15	0.210
304	4.79	0.800	334	0.17	0.170
305	4.94	0.790	335	0.02	0.130
306	3.02	0.790	336	0.17	0.083
307	1.16	0.790	337	0.32	0.038
308	2.18	0.780	338	1.93	0.000
309	2.25	0.770	339	2.15	0.000
			340	1.07	0.000

Table 2-5. Absorption cross sections and quantum yields for formaldehyde photolysis to stable products:



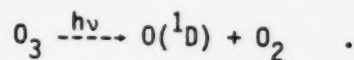
Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	2.34	0.440	320	1.71	0.390
281	1.65	0.420	321	1.32	0.410
282	0.76	0.400	322	0.43	0.430
283	0.46	0.380	323	0.60	0.460
284	3.93	0.370	324	0.75	0.490
285	3.46	0.350	325	2.19	0.510
286	2.32	0.330	326	3.44	0.540
287	0.95	0.320	327	1.75	0.550
288	2.32	0.300	328	1.01	0.570
289	2.50	0.290	329	3.03	0.580
290	1.43	0.280	330	1.96	0.590
291	1.32	0.270	331	0.79	0.600
292	0.66	0.250	332	0.32	0.610
293	5.22	0.240	333	0.15	0.620
294	4.30	0.240	334	0.17	0.620
295	3.21	0.230	335	0.02	0.620
296	1.59	0.220	336	0.17	0.620
297	1.96	0.210	337	0.32	0.620
298	3.66	0.210	338	1.93	0.610
299	1.55	0.210	339	2.15	0.610
300	0.72	0.200	340	1.07	0.600
301	1.51	0.200	341	0.31	0.590
302	0.74	0.200	342	0.94	0.570
303	4.35	0.200	343	1.37	0.560
304	4.79	0.200	344	0.57	0.540
305	4.94	0.210	345	0.12	0.520
306	3.02	0.210	346	0.04	0.500
307	1.16	0.210	347	0.04	0.470
308	2.18	0.220	348	0.07	0.450
309	2.25	0.230	349	0.03	0.420
310	1.03	0.240	350	0.03	0.390
311	0.81	0.250	351	0.09	0.360
312	1.49	0.260	352	0.90	0.330
313	1.55	0.270	353	1.17	0.300
314	3.99	0.280	354	0.72	0.260
315	2.88	0.300	355	0.26	0.230
316	2.79	0.310	356	0.05	0.200
317	3.59	0.330	357	0.03	0.160
318	1.65	0.350	358	0.04	0.130
319	0.73	0.370	359	0.03	0.100

Table 2-6. Absorption cross sections and quantum yields for ozone photolysis to $O(^1D)$:



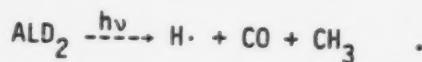
Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	397.00	0.900	300	39.20	0.900
281	360.00	0.900	301	34.40	0.900
282	324.00	0.900	302	30.30	0.900
283	301.00	0.900	303	26.30	0.900
284	273.00	0.900	304	23.50	0.900
285	244.00	0.900	305	20.20	0.884
286	221.00	0.900	306	18.00	0.848
287	201.00	0.900	307	15.60	0.800
288	176.00	0.900	308	13.60	0.740
289	158.00	0.900	309	12.30	0.660
290	141.00	0.900	310	10.30	0.560
291	126.00	0.900	311	9.27	0.450
292	110.00	0.900	312	8.00	0.340
293	98.90	0.900	313	6.92	0.250
294	86.20	0.900	314	6.29	0.180
295	76.70	0.900	315	5.22	0.120
296	66.40	0.900	316	4.78	0.080
297	58.80	0.900	317	4.04	0.050
298	51.00	0.900	318	3.72	0.020
299	45.20	0.900	319	2.91	0.000

Table 2-6. Absorption cross sections and quantum yields for ozone photolysis to $O(^1D)$:



Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	397.00	0.900	300	39.20	0.900
281	360.00	0.900	301	34.40	0.900
282	324.00	0.900	302	30.30	0.900
283	301.00	0.900	303	26.30	0.900
284	273.00	0.900	304	23.50	0.900
285	244.00	0.900	305	20.20	0.884
286	221.00	0.900	306	18.00	0.848
287	201.00	0.900	307	15.60	0.800
288	176.00	0.900	308	13.60	0.740
289	158.00	0.900	309	12.30	0.660
290	141.00	0.900	310	10.30	0.560
291	126.00	0.900	311	9.27	0.450
292	110.00	0.900	312	8.00	0.340
293	98.90	0.900	313	6.92	0.250
294	86.20	0.900	314	6.29	0.180
295	76.70	0.900	315	5.22	0.120
296	66.40	0.900	316	4.78	0.080
297	58.80	0.900	317	4.04	0.050
298	51.00	0.900	318	3.72	0.020
299	45.20	0.900	319	2.91	0.000

Table 2-7. Absorption cross sections and quantum yields for acetaldehyde photolysis to radical products:



Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield	Wavelength (nm)	Cross Section (cm ² /molec.) (x 1.E+20)	Quantum Yield
280	4.50	0.580	305	3.40	0.370
281	4.54	0.575	306	3.27	0.350
282	4.58	0.570	307	3.14	0.330
283	4.62	0.565	308	3.01	0.310
284	4.66	0.560	309	2.88	0.290
285	4.70	0.555	310	2.75	0.270
286	4.74	0.550	311	2.62	0.250
287	4.78	0.545	312	2.49	0.230
288	4.82	0.540	313	2.36	0.210
289	4.86	0.535	314	2.23	0.190
290	4.90	0.530	315	2.10	0.170
291	4.82	0.520	316	2.04	0.156
292	4.74	0.510	317	1.98	0.142
293	4.66	0.500	318	1.92	0.128
294	4.58	0.490	319	1.86	0.114
295	4.50	0.480	320	1.80	0.100
296	4.46	0.470	321	1.66	0.088
297	4.42	0.460	322	1.52	0.076
298	4.38	0.450	323	1.38	0.064
299	4.34	0.440	324	1.24	0.052
300	4.30	0.430	325	1.10	0.040
301	4.12	0.418	326	1.18	0.032
302	3.94	0.406	327	0.94	0.024
303	3.76	0.394	328	0.85	0.016
304	3.58	0.382	329	0.77	0.008
			330	0.69	0.000

Table 2-8. SAI and UNC j-value calculations for Peterson (1977) actinic flux corrected to 640 m (Demerjian et al., 1980) and slightly different albedos.

Zenith Angle (deg)	SAI absolute photolysis rates ($\times 1000, \text{min}^{-1}$, albedo = 0.05)			UNC absolute photolysis rates ($\times 1000, \text{min}^{-1}$, albedo = 0.08)			
	HCHOr	HCHOs	OLD ALD2	HCHOr	HCHOs	OLD ALD2	
0	1.811	2.164	2.770	2.179	3.391	2.715	0.347
10	1.785	2.138	2.691	2.141	3.353	2.620	0.338
20	1.705	2.055	2.440	2.036	3.237	2.362	0.314
30	1.556	1.929	2.023	1.858	3.032	1.962	0.275
40	1.339	1.730	1.532	1.599	2.724	1.463	0.222
50	1.062	1.457	1.011	1.272	2.304	0.944	0.161
60	0.722	1.095	0.503	0.873	1.732	0.462	0.096
70	0.366	0.644	0.156	0.448	1.034	0.140	0.041
78	0.138	0.284	0.036	0.172	0.466	0.030	0.012
86	0.020	0.055	0.003	0.043	0.127	0.003	0.002

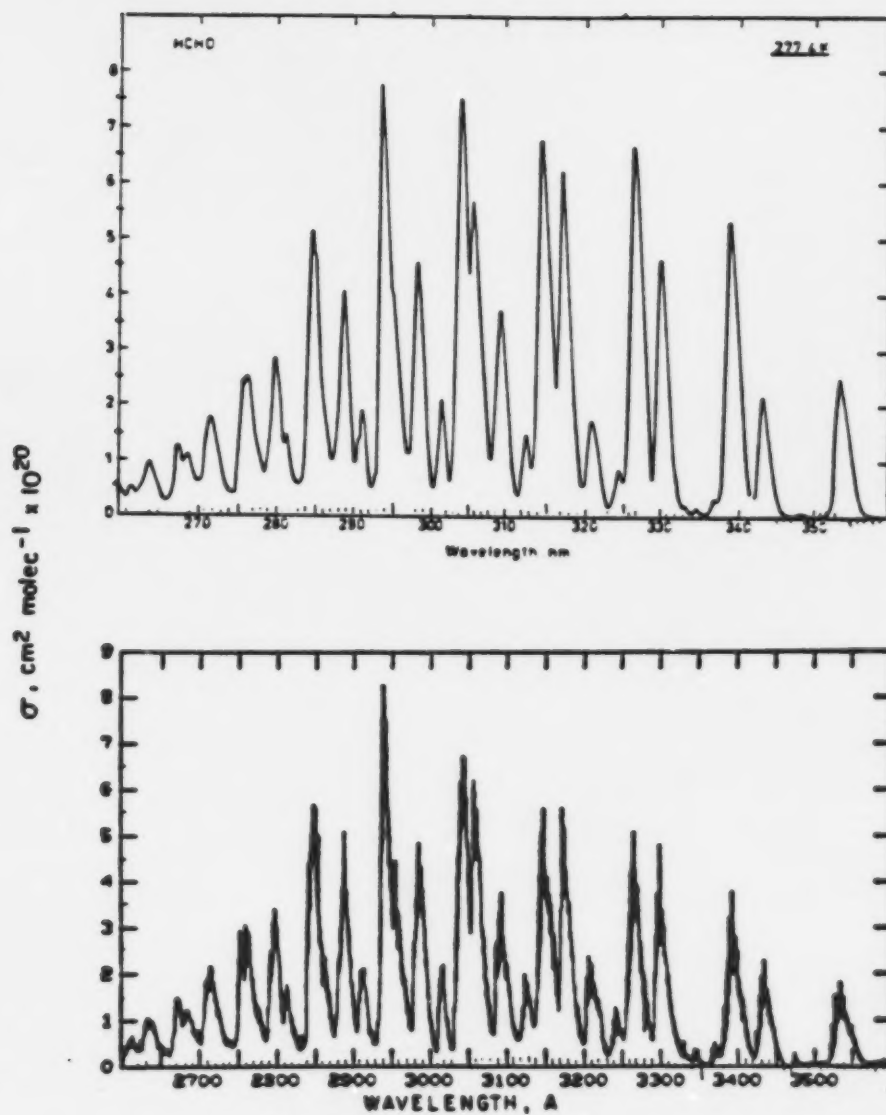


FIGURE 2-12. Comparison of absorption cross sections for formaldehyde Moortgat (top) and Bass (bottom).

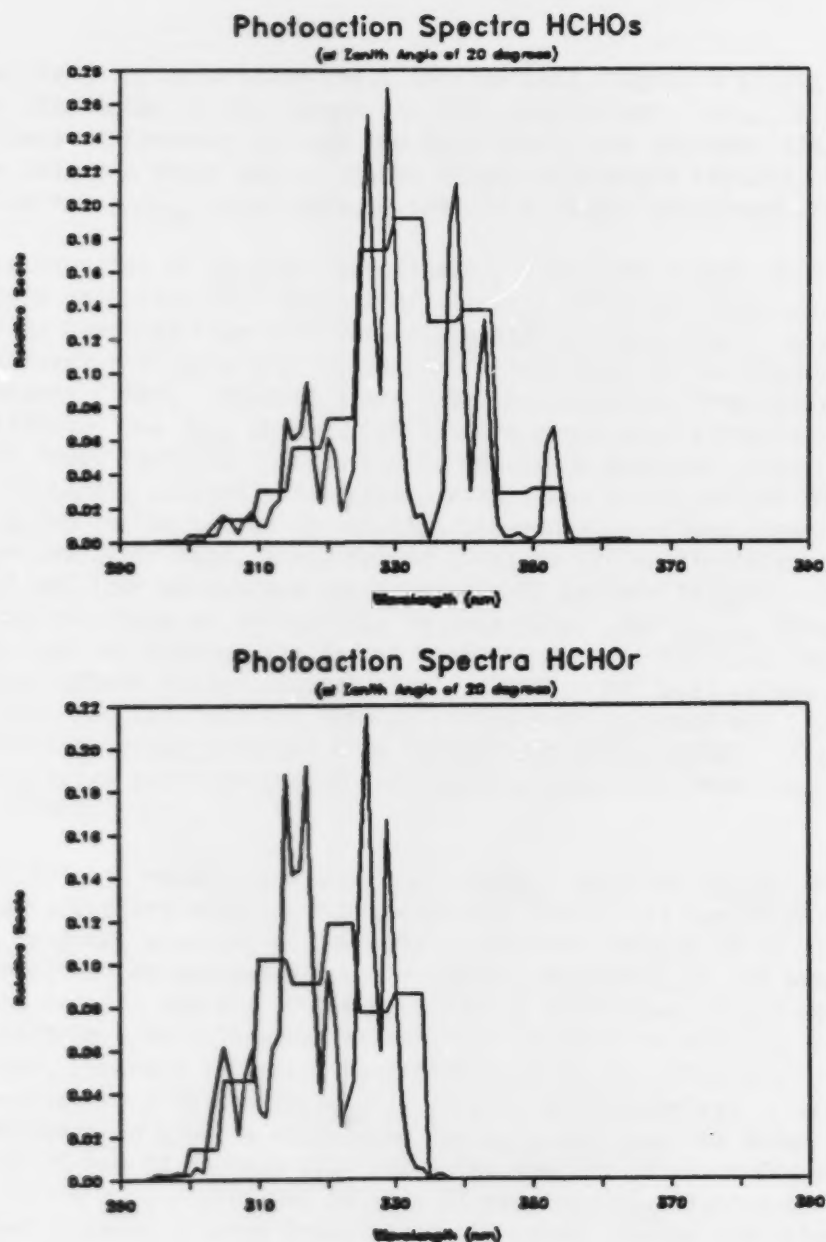


FIGURE 2-13. Photoaction spectra for formaldehyde to stable products (top) and formaldehyde to radicals (bottom) using the 10 nm bins of NASA (DeMore, 1985) and the 1 nm bins of Bass (1980).

quantum yield and absorption cross-section data, though a slight error can also be attributed to the larger bin size used by UNC. Also, since the significant differences between the Bass (1980) and Moortgat (1986) cross-section data are found mainly in the longer wavelength regions, larger variation for J_{HCHO} s occur because that is a longer wavelength process.

Our determination of $J_{\text{O}_1\text{D}}$ is approximately 5 percent higher than that of UNC, again resulting from the use of slightly different data sources. Our absorption cross-section data were calculated by obtaining 1 nm averages of high-resolution data provided by Dr. Arnold Bass of the National Bureau of Standards (1986). Quantum yield data were obtained from Atkinson and Lloyd (1984). The $J_{\text{O}_1\text{D}}$ photoaction spectra occur over a smaller region and have fewer features than do the formaldehyde spectra. Also, there is less uncertainty currently associated with these cross-section data. This is reflected in the better correlation between $J_{\text{O}_1\text{D}}$ values shown in Table 2-8. On the other hand, acetaldehyde j -values differ significantly from those of UNC (our values are approximately 20 percent larger). This again indicates the range of variability in data sets. Our J_{ALD_2} values were derived from the quantum yields and absorption cross sections reported in the latest CODATA review (Baulch et al., 1984). UNC used values from Carter (1986), who utilized the quantum yields from Atkinson and Lloyd (1984) and absorption cross sections from Calvert and Pitts (1966). Figure 2-14 shows the differences in photoaction spectra resulting from these different values.

These photolysis rates, namely J_{HCHO} , J_{HCHO} s, $J_{\text{O}_1\text{D}}$ and J_{ALD_2} , represent the important short-wavelength tropospheric photolysis reactions. Each process responds somewhat differently to diurnal changes in solar spectra (as represented by changes in zenith angle), depending on the proximity of their photoaction spectra to the more highly attenuated blue side of the solar spectrum. Recalling the differences in solar irradiance shown in Figure 2-9, Figure 2-15 shows the differences in the relationship of these short wavelength j -values to J_{NO_2} at varying zenith angles. Figure 2-16 shows photoaction spectra calculated for $J_{\text{O}_1\text{D}}$ and J_{NO_2} , at solar zenith angles of 20 and 60 degrees (for the solar spectra shown in Figure 2-10). While J_{NO_2} diminishes by only 37 percent, $J_{\text{O}_1\text{D}}$ decreases by over 80 percent because a large fraction of the higher energy radiation needed for $\text{O}(^1\text{D})$ production (below 300 nm) is not available at zenith angles of 60 degrees due to the increases in atmospheric optical thickness and effective ozone column density with zenith angle.

In addition to the determination of these values, we undertook a brief investigation of the bin width needed to accurately determine the j -value through numerical integration methods. The appropriate bin width is usually determined by the presence of fine structure in one or more of the functions whose product is being integrated. For the species considered

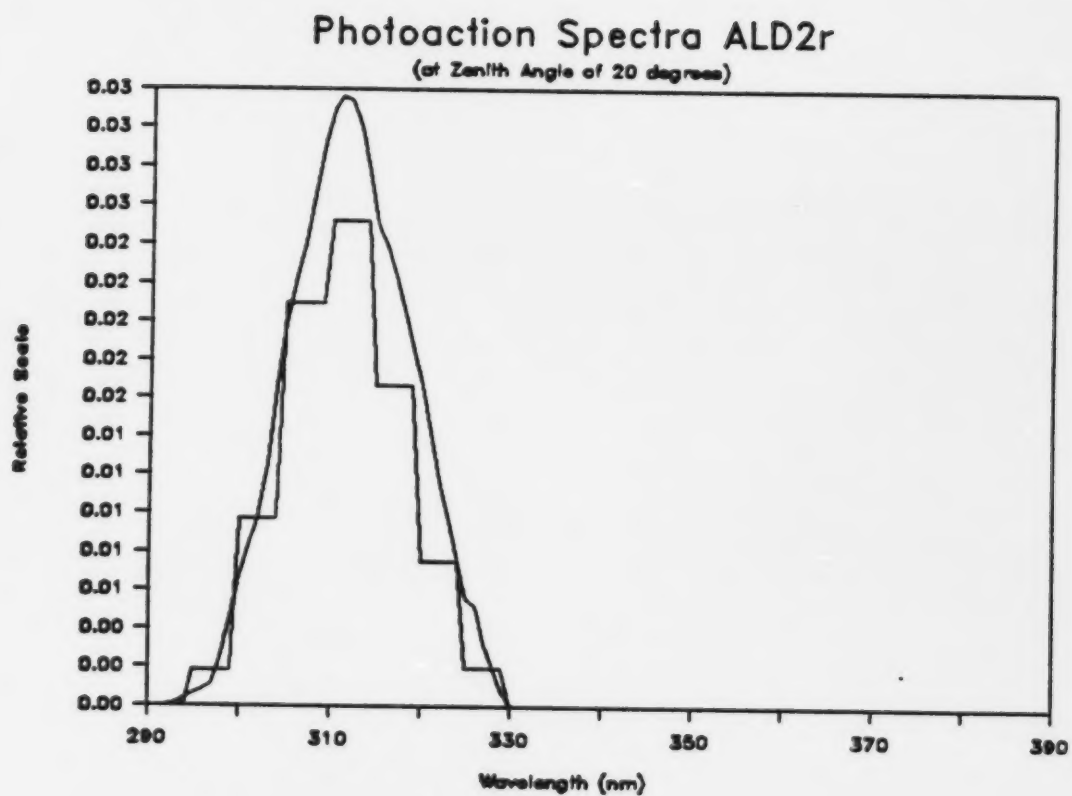


FIGURE 2-14. Photoaction spectra for acetaldehyde using 1 and 5 nm bins.

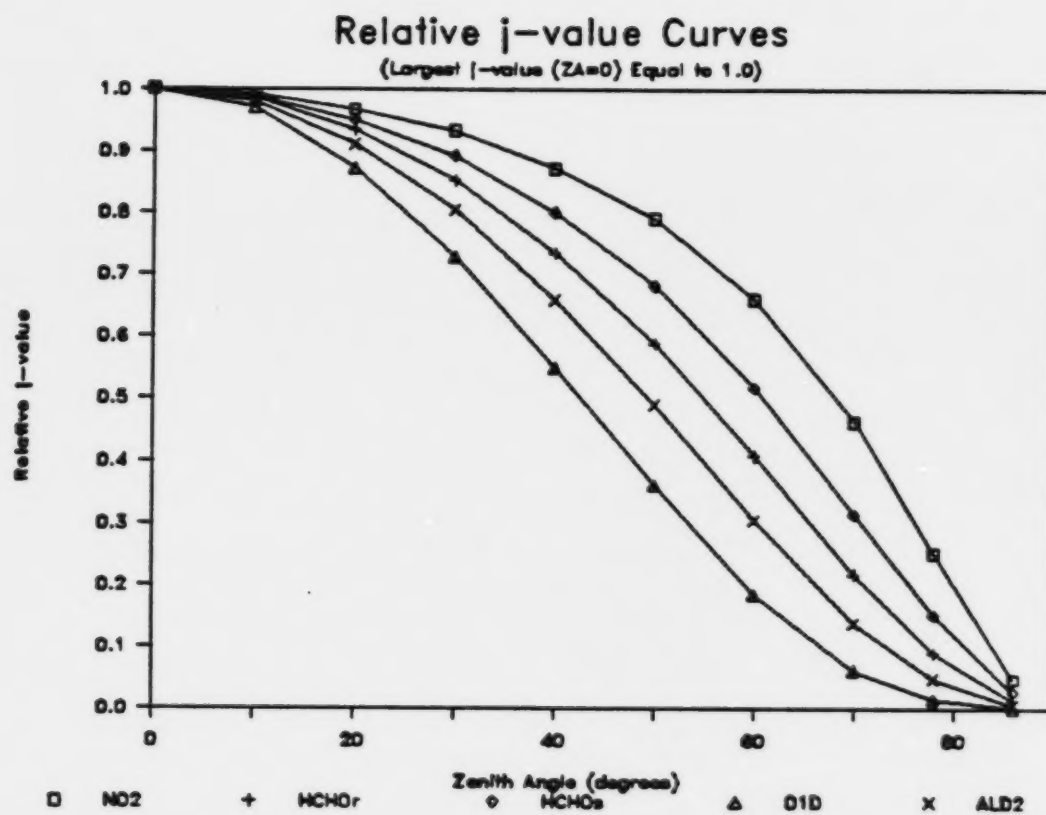


FIGURE 2-15. Comparison of relative j-value curve shapes with respect to solar zenith angle for the five major photolytic species.

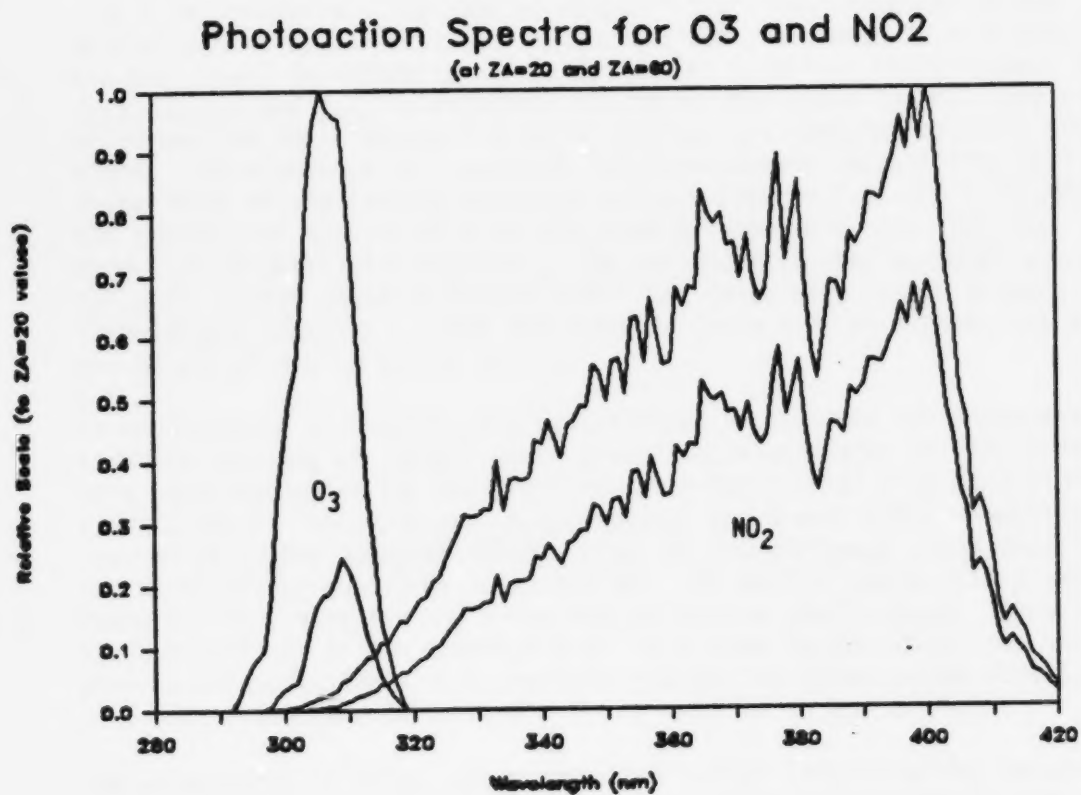


FIGURE 2-16. Comparison of photoaction spectra for J_{NO_2} and J_{O_3} for 20 and 60 degree solar zenith angles.

here, the finest structure occurs in the absorption cross-section data, though some structure is also seen in the actinic flux data. Both the quantum yield and actinic flux data, however, have been less highly resolved than the cross sections (which are usually available in fractions of nm bins), though it is assumed that their functions should be somewhat smoother. Of the photoaction spectra shown thus far, the formaldehyde curves had more distinct features, occurring irregularly at approximately 4 or 5 nm intervals. The lack of resolution of these features during multiplication by the actinic flux and quantum yield data in each specific bin may result in averaging errors during the numerical integration. The j_{O_1D} , j_{ALD2} , and j_{NO_2} calculations should be less prone to this type of error because their absorption cross sections are somewhat smoother functions. Therefore, we will consider the formaldehyde calculations here as an estimate of the largest potential error. Figures 2-17 and 2-18 compare the photoaction spectra of 1 nm with that of other bin sizes for both formaldehyde photolysis channels. The actinic flux used was that shown for a 20° zenith angle in Figure 2-10. The calculated values of both formaldehyde photolysis rates are shown in Table 2-9 for various bin sizes and 20 and 60 degree zenith angles.

As we discussed previously, our calculations of j-values for photochemical kinetics modeling of various urban areas (addressed later in this report) were performed using the more resolved extraterrestrial flux data of WRC (Iqbal, 1983). In addition, the Schippnick and Green (1982) algorithm was used to calculate spectral actinic flux for the different urban locations and altitudes (ground-level plus 640 m). The optical depth data given in Table 2-1 were used for the different extinction coefficients. Because these conditions differ somewhat from those used in the comparison and error assessment, Table 2-10 presents results for ozone column densities of 0.300, 0.250, and 0.200 cm-atm for a location at sea level.

The uncertainty in these values and other values calculated for locations of higher elevation develops primarily because of uncertainty in the three variables needed to determine photolysis rates, namely, actinic flux, absorption cross section, and quantum yield. For ozone photolysis to $O(^1D)$, the absorption cross-section data appear to be within about 10 percent agreement (Baulch et al., 1984), while the quantum yield data are well-characterized but lacking for some critical regions. The uncertainty could be as high as 20 percent in a few specific areas. The greatest uncertainty associated with the calculation of j_{O_1D} is the variability of actinic flux in the narrow, high-energy region of the surface solar spectrum where the ozone photoaction spectrum exists. We discussed previously an uncertainty in the extraterrestrial flux data of as high as 25 percent in some bins within this region. Because it is located at the surface ultraviolet cutoff, this j-value is also the most sensitive to changes in

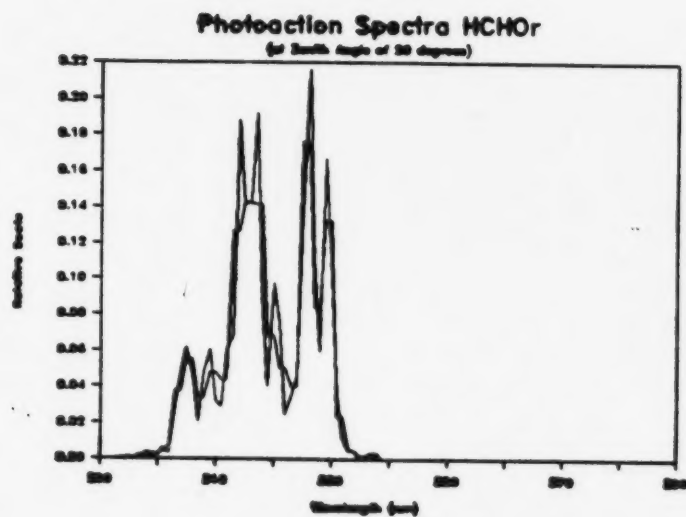
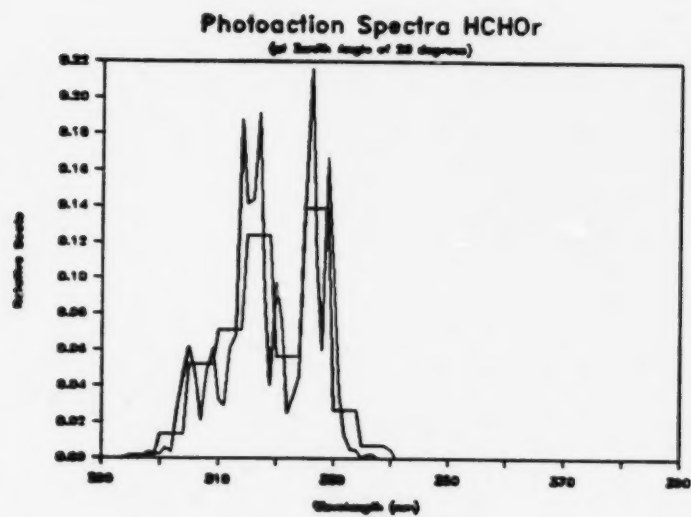
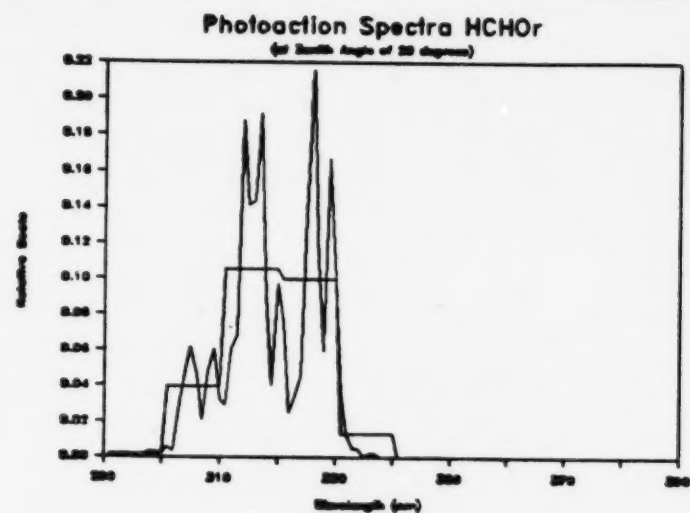


FIGURE 2-17. Comparison of 1 nm photoaction spectra for HCHO_r with spectra calculated with 10 (top), 5 (middle), and 1 nm (bottom) bins.

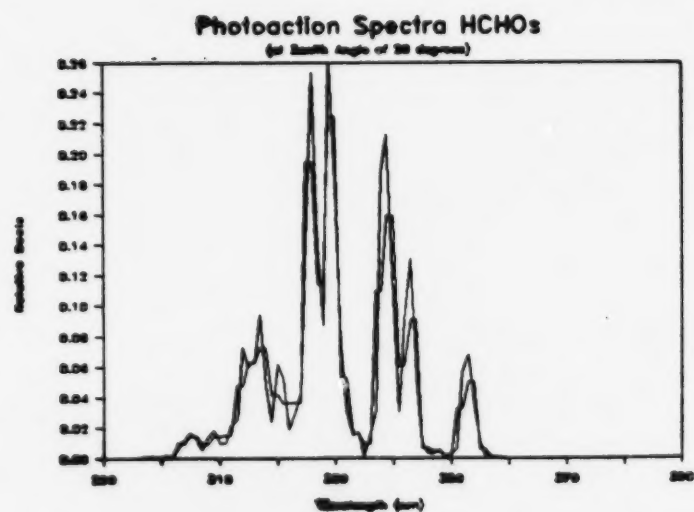
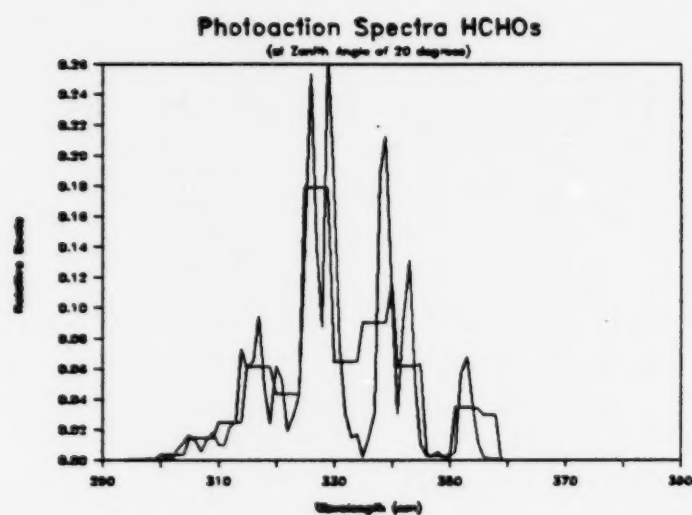
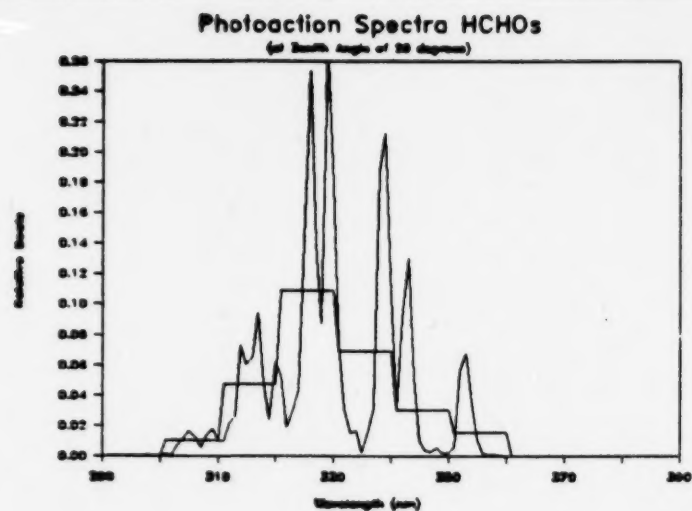


FIGURE 2-18. Comparison of 1 nm photoaction spectra for HCHO_s with spectra calculated with 10 (top), 5 (middle), and 1 nm (bottom) bins.

TABLE 2-9. J-values ($\times 1000, \text{min}^{-1}$) calculated for formaldehyde photolysis at different bin sizes (albedo = 0.05, altitude=0, ozone column = 0.300 cm-atm).

Bin Size (nm)	Zenith Angle = 20		Zenith Angle = 60	
	J _{HCHO} r	J _{HCHO} s	J _{HCHO} r	J _{HCHO} s
1	1.470	1.803	0.592	0.905
2	1.471	1.801	0.592	0.903
5	1.475	1.872	0.601	0.947
10	1.555	1.700	0.632	0.842

Relative Error (percent):

1	0.000	0.000	0.000	0.000
2	0.052	-0.110	0.039	-0.121
5	0.354	3.828	1.471	4.645
10	5.810	-5.719	6.830	-6.970

Table 2-10. Results of j-value calculations WRC extraterrestrial flux (Iqbal, 1983) and Schipnick and Greene actinic flux formulation. Albedo is 0.08 and altitude is 640 m.

Absolute photolysis rates at 640 m
($\times 1000, \text{min}^{-1}$, albedo = 0.08)

Zenith Angle (deg)	0.300 cm-atm			ALD2	0.250 cm-atm			ALD2	0.200 cm-atm			ALD2
	HCHOr	HCHOs	OID		HCHOr	HCHOs	OID		HCHOr	HCHOs	OID	
0	2.06	2.54	2.45	0.448	2.22	2.61	3.25	0.521	2.43	2.68	4.49	0.621
10	2.02	2.51	2.37	0.437	2.19	2.58	3.14	0.509	2.39	2.65	4.35	0.608
20	1.94	2.44	2.14	0.410	2.10	2.51	2.86	0.481	2.30	2.58	3.97	0.573
30	1.78	2.30	1.78	0.364	1.93	2.37	2.39	0.427	2.12	2.44	3.36	0.512
40	1.56	2.10	1.33	0.303	1.70	2.16	1.82	0.356	1.87	2.23	2.58	0.430
50	1.28	1.82	0.860	0.228	1.40	1.88	1.20	0.272	1.55	1.94	1.75	0.331
60	0.920	1.42	0.432	0.146	1.01	1.47	0.625	0.176	1.13	1.52	0.947	0.217
70	0.506	0.888	0.139	0.067	0.562	0.920	0.213	0.083	0.633	0.956	0.344	0.105
78	0.202	0.409	0.033	0.023	0.227	0.425	0.053	0.028	0.258	0.444	0.090	0.037
86	0.028	0.071	0.003	0.003	0.032	0.074	0.005	0.003	0.036	0.077	0.009	0.004

diurnal variables that depend on zenith angle (and atmospheric optical thickness). Therefore, assuming 10, 15 and 20 percent associated overall errors, respectively, for cross section, quantum yield, and actinic flux data, the root mean square error is slightly greater than 50 percent, with higher values occurring at very large zenith angles because of the increasing uncertainty of actinic flux calculations for this region.

Calculation of formaldehyde j -values benefits from the fact that these two processes occur at longer wavelengths than does the $O(^1D)$ -forming channel of ozone photolysis. This provides more certain extraterrestrial and actinic flux values, and the j -values are less sensitive to changes in zenith angle. Unfortunately, because they have been investigated less thoroughly, the other variables are not as certain as the ozone variables. We have discussed the error associated with absorption cross-section and quantum yield data. Our calculations show that the use of different, equally acceptable quantum yield data with typical actinic flux and cross section data gives results that differ by about 10 percent. In addition, the available absorption cross-section data differ by 30 percent over large spectral regions. If we assign an arbitrary actinic flux error of 10 percent and assume that calculations are performed in small enough bins to minimize averaging error (see below), the root mean square error is about 60 percent.

Acetaldehyde and higher formaldehydes have less fine structure in their absorption cross sections, but the acetaldehyde absorption cross sections are far less certain than the formaldehyde and ozone values. In addition, the quantum yield data are sparse and the photoaction spectrum occurs in the same region as that of ozone (forming $O(^1D)$), leading to greater uncertainty than occurs in similar formaldehyde calculations. Because of these conditions, it is difficult to place a numerical value on the error bands of J_{ALD2} . We arbitrarily assume an associated error 100 percent for calculation of J_{ALD2} for all diurnal conditions, though less error should be associated with values calculated at lower zenith angles. Fortunately, the rate of acetaldehyde photolysis is significantly slower than that of formaldehyde, and far less acetaldehyde is produced during photochemical reactions in the atmosphere.

There is also a smaller error associated with the methodology utilized in the calculation of j -values. It is our suggestion that 10 nm bins not be used in the calculation of j -values unless absolutely necessary because of minimal data availability. The resolution of extraterrestrial flux in 2 nm bins, combined with absorption cross-section data of even finer resolution, necessitates the calculation of j -values at intervals of that size or smaller. We have shown that calculations in 5 nm bins for formaldehyde (which has a distinct fine structure at a peak width of about 2 nm) lose

accuracy when compared with 2 nm calculations. Therefore, we recommend the calculation of photolysis rates at 2 nm intervals or less to ensure that averaging of higher resolution data does not produce errors.

Comparison of Model Calculations with Direct Measurements

The simulations discussed in Section 3 (modeling) attempt to ascertain the relative changes in urban photochemical conditions due to depletion of ozone column densities by a fixed amount. We chose 0.300 cm-atm as a general present-day base case, and reduced that column twice by 0.050 cm-atm (16.67 percent) to provide the two future scenarios of 0.250 and 0.200 cm-atm. Before utilizing the j -values calculated from the modeled actinic fluxes, however, it was necessary to verify that these calculations were realistic for the conditions simulated. We compared our calculated rates to chemical actinometry measurements at different ozone column densities and solar zenith angles. This is a very useful test because the measured actinometry value is the j -value, a real rate that can be directly compared to the results of model calculations. In addition, because the effective ozone column value accounts for increasing atmospheric thickness with decreasing solar elevation, this value is always larger than the overhead column. Hence, there are only a few future effective ozone column conditions for very high solar elevations and low overhead column densities that have not had comparable measurements performed under present conditions of similar effective ozone column densities (from a somewhat different combination of zenith angles and overhead column densities). In addition, the future values outside the present range should be extrapolations of the present relationship between effective ozone column and j -values. In the following discussion, we compare measured j -values and effective ozone column pairs with predicted pairs for a range of overhead columns.

Over the previous decade, actinometry measurements for the $O(^1D)$ -forming channel of ozone photolysis have become increasingly rigorous. Unfortunately, many of the earlier j_{O1D} studies and the few available aldehyde studies did not measure ozone column density and solar zenith angle; therefore, they are not useful in assessing the ability of our model to accurately predict changes in j -values caused by changes in these variables. However, the more recent j_{O1D} actinometry data are sufficiently complete for verifying that the model values of actinic flux are correctly calculated in the shorter wavelength regions. Therefore, we concentrate our evaluation efforts on comparisons with these data sets.

The earliest data sets of j_{O1D} are ground-level measurements performed by Bahe et al. (1979b) and Dickerson et al. (1982). These data are shown at the top of Figure 2-19, with the results of Bahe and coworkers appearing

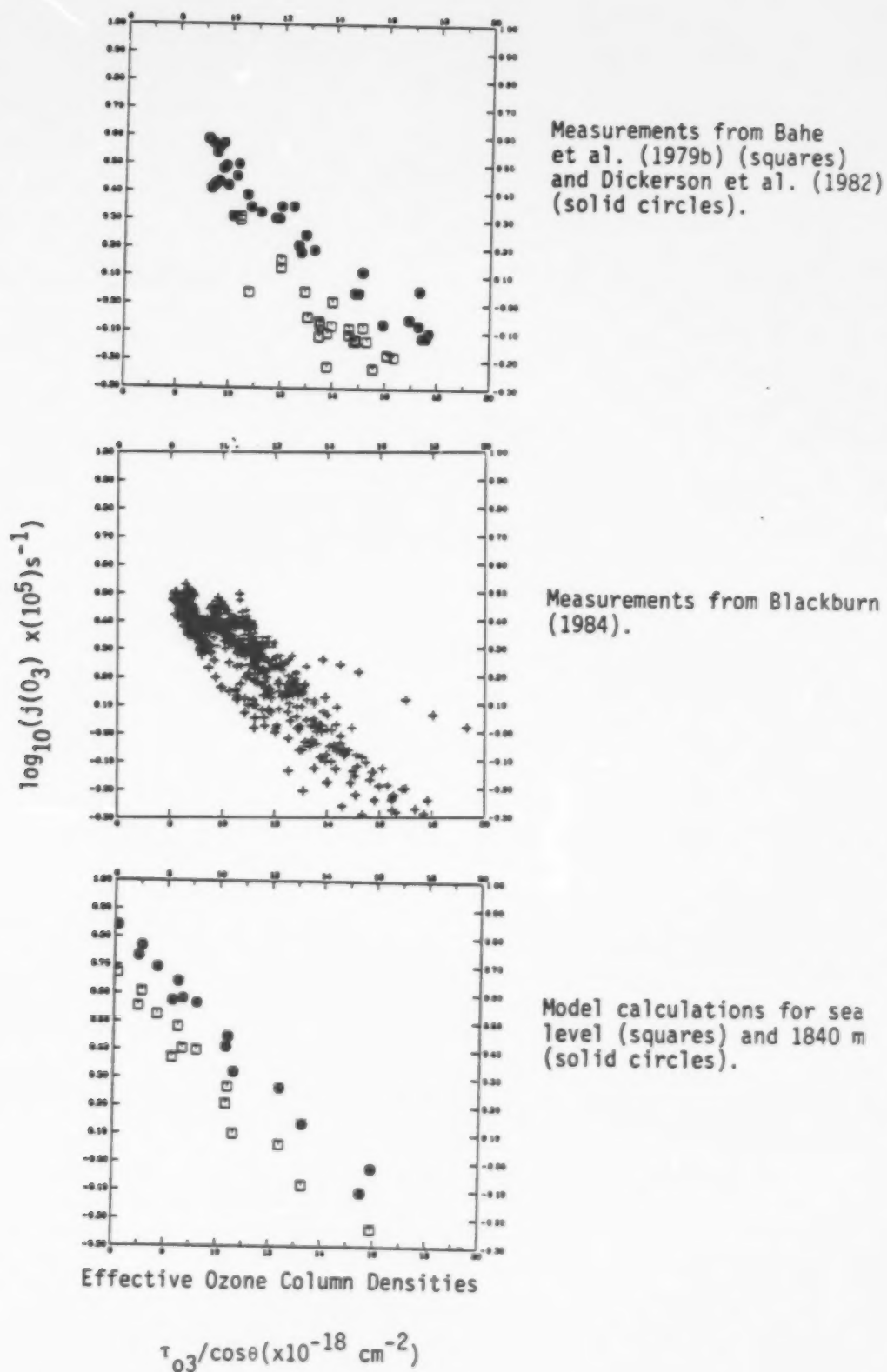


FIGURE 2-19. Comparison of measured and calculated j_{010} values.

as squares. As Dickerson and coworkers (1982) point out, the locations in which these two sets of measurements were made differ significantly and probably caused some differences in the results. The measurements of Bahe et al. were done in the heavily industrialized Ruhr-Rhine Valley of West Germany, where air pollution episodes are common; some decrease in surface j -values could be expected due to this influence. The data of Dickerson et al. (1982) were collected in Boulder, Colorado, an area of limited clouds, high summer temperatures, relatively clean air and, most important, an elevation of about 1800 m. An estimate* of the relative difference in actinic flux for the 305 to 315 nm bin at 40 degree zenith angle indicates an expected increase of about 50 percent at the higher elevation. This translates into a difference of about 0.2 on the log J_{010} scale of Figure 2-19, and indicates that the somewhat higher j -values measured by Dickerson et al. (1982) compare quite well with those of Bahe et al. (1979b) once environmental conditions are considered.

A far more complete set of surface J_{010} measurements, including ozone column density and aerosol optical depths, was compiled by Blackburn (1984). These data were collected at the University of Michigan for 75 days between May and July. The results of these measurements are also shown in Figure 2-19. The main sequence of points is in a region similar to that of Bahe et al. and is slightly lower than the numbers of Dickerson and coworkers. This coincides with the foregoing argument, since the Michigan elevation is also lower than the measurement site in Colorado. The six outlying points are measurements at either low aerosol loading or very high zenith angles (Blackburn, 1984).

The results of our model predictions for J_{010} at 0.300, 0.250 and 0.200 cm-atm are shown at the bottom of Figure 2-19. Squares represent near-sea-level values and circles were calculated at 1840 m elevation to facilitate comparison with the data of Dickerson et al. (1982). Our two sets of values are not precisely linear because the $1/\cos(\theta)$ correction is not exact (see Blackburn, 1984). Our predictions compare favorably with the data of both Blackburn (1984) and Bahe et al. (1979b) for the near-sea-level predictions, and Dickerson et al. (1982) for the 1800 m values. As noted, our predictions extend to lower effective ozone column values and larger j -values due to the inclusion of potential decrease in future overhead ozone columns. We also include results beginning at zenith angles of 20 degrees and less, whereas the measurements of most researchers rarely exceeded 30 degrees. Therefore, extrapolation of these measurements must be performed to verify our predictions of future, low, effective ozone column conditions.

* Based on the model results of Demerjian et al, (Schere, 1986).

We feel that, in all cases, these comparisons are favorable. Although there are no similar chemical actinometry data for the formaldehyde and acetaldehyde photolysis reactions, this evaluation indicates that our calculation method for the prediction of future actinic flux is valid; therefore, the errors associated with the calculation of j-values for these aldehydes should be mainly based on the uncertainties of their experimentally determined absorption cross-section and quantum yield data, as described earlier.

SECTION 3

SIMULATION OF URBAN PHOTOCHEMISTRY UNDER CONDITIONS OF FUTURE GLOBAL CHANGE

The goal of this phase of the study was to investigate the potential changes in urban oxidant formation caused by possible future alterations in global climate. More specifically, we were interested in (1) additional photochemical reactivity and (2) the amount of oxidant formation that could occur as a result of future increases in surface temperature and decreases in stratospheric ozone (increases in surface ultraviolet irradiance and photolysis rates). Most photochemical kinetics modeling performed in this phase involved the simulation of at least six urban trajectories, covering as wide a range of locations and pollution precursor conditions as possible; the primary objective was to provide information on potential changes in urban ozone production due to future changes in stratospheric ozone concentrations and surface temperature ranges.

Three different ozone column densities and temperature ranges were used in the future scenario calculations. The results of photochemical kinetics models were used to elucidate important dynamic processes that might occur with changing conditions. It was envisioned that, in addition to changes in ozone production, other indicators such as concentrations of hydrogen peroxide, hydroxyl radicals, and various nitrogen-containing species would also provide key information on possible alterations to urban atmospheric chemical dynamics. In addition to the single-day city scenarios, we studied multi-day impacts for two cities--one that had attained the National Ambient Air Quality Standard (NAAQS) for ozone, and one in non-attainment status. A second photochemical kinetics mechanism was used in one set of simulations to verify that the results were not mechanism-specific.

In this investigation of future urban impacts, we felt it appropriate to use the OZIPM photochemical trajectory model since, when combined with the EKMA procedure, that model is most often employed to determine the amount of non-methane organic carbon (NMOC) reduction needed to achieve compliance with the ozone NAAQS of 0.12 ppm. EKMA calculations can also aid in providing estimates of atmospheric and emission conditions expected in future scenarios. Therefore, we have used OZIPM/EKMA and available input

data from different State Implementation Plans (SIPs) to directly address the regulatory impact of these anticipated global changes. The models and chemical mechanisms used are briefly described next, followed by a discussion of the modeling protocol, input data, and results.

DESCRIPTION OF MODELS AND MECHANISMS USED

The air quality simulation model used in this study was the OZIPM-3 trajectory model described in Hogo and Whitten (1985). This model, in combination with the Empirical Kinetic Modeling Approach (EKMA), has been extensively used in Level-III, city-specific ozone modeling for SIPs. It employs the CHEMK routine (Whitten and Hogo, 1980) for solution of the partial differential equations representing the chemical species and mechanism for each simulation. This routine is based on the higher order, predictor-corrector method of Gear (1971) and is a very accurate solution scheme for modeling stiff atmospheric chemistry systems. With OZIPM-3, different chemical kinetic mechanisms can be easily input, eliminating the need for complex coding of a second mechanism.

The OZIPM-3 model allows input of most key variables that affect the chemistry of urban simulations. Of particular importance for this study, hourly temperature values and variable photolysis rates (with zenith angle and ozone column density), the key parameters for testing sensitivity, can be input. Such parameters as initial concentrations, transported concentrations, aloft concentrations, inversion height profile, organic reactivity, emissions, and photolytic effects due to location of a specific city are also variable. These variables allow the simulation of different city-specific scenarios such as the ones available to us from past SIPs.

In the preceding section, we described the basis, procedure, and uncertainties for our calculation of middle ultraviolet surface spectral irradiance. These calculations were based on the method of Schippnick and Green (1982) and the extraterrestrial flux data of the World Radiation Center (WRC) [Iqbal, 1983]. From these calculations, we determined the appropriate j -values for all photolytic species (and thus, the OZIPM-3 input values) needed to simulate the effects of different ultraviolet intensities for three different future ozone column densities. Since these values are necessarily zenith-angle-dependent, such calculations were performed for each study location because each city has a different longitude, latitude, and elevation. As described in Section 1, the selected ozone column densities were 0.300 (base case), 0.250, and 0.200 cm-atm.

The primary photochemical kinetics mechanism used in this study was the CBM-X developed by Whitten et al. (1985) and implemented in the OZIPM-3 by Hogo and Whitten (1985). A listing of this mechanism is provided in Table 3-1; the reader is referred to the referenced works for a complete model description we initially envisioned the alternate mechanism as that of Atkinson et al. (1982). However, since the newer CALL (Lurman et al., 1987) and CBM-IV mechanisms (Gery et al., 1987) have recently become available for OZIPM-type models, we selected one of these instead. Although the CBM-IV is very different from the CBM-X mechanism, we chose the CALL mechanism to ensure that we had selected an obviously unrelated mechanism for this test. That mechanism is listed in Table 3-2; the reader is referred to Lurman et al. (1987) and the references therein for a more complete description of the mechanism. The listing in Table 3-2 contains a few updates from the referenced report. We advise all those attempting to use a chemical kinetics mechanism, whether it be the CBM-X, ALW, CALL, CBM-IV, or another, to contact the developer or project officer to obtain the most recent and error-free source possible at the outset of a study.

From the listings given in Tables 3-1 and 3-2, it is apparent that these mechanisms are condensed versions of more explicit chemical mechanisms. Both were developed from nearly the same fundamental data bases of basic kinetic and stoichiometric data, and were evaluated and further developed on the basis of smog chamber simulations. The primary focus in the development of both mechanisms has been the prediction of oxidant formation in urban-type scenarios. The CBM-X and CALL mechanisms are not, however, duplicates of one another. In addition to the use of somewhat different assumptions concerning inorganic reactions, two different methodologies have been used to describe the highly complex organic portions of each mechanism. The CBM-X "lumps" structural groups, whereas the CALL lumps molecular entities. Therefore, though these mechanisms represented the state-of-the-science at the time that the mechanism comparison portion of this study was performed, they use two different approaches and perfect agreement between their predictions should not be expected. Conversely, similar predictions in future trends by both mechanisms should be considered a strong argument for a good mechanistic description of the future chemical dynamics as implemented in the test scenario in OZIPM-3.

MODELING PROTOCOL

There are a number of possible protocols for the use of existing urban data sets to investigate potential future changes. The key procedure in any such study is the method used to determine future conditions. That is, a reasonable protocol requires a justifiable transition rationale for

TABLE 3-1. OZIPM-3 Listing of the CBM-X Mechanism.

Reaction Number	Mechanism			k ₂₉₈ (ppm ⁻¹ min ⁻¹)	Activation Energy (E/R)
1	N02	=	N0 +	1.000E 00	0.000E-01
2	0	=	03	4.440E 06	-6.900E 02
3	03	=	N02	2.660E 01	1.430E 03
4	0	=	N0	1.380E 04	0.000E-01
5	0	=	N02	2.320E 03	-6.000E 02
6	0	=	N0	3.120E 03	-4.110E 02
7	N02	=	N03	4.740E-02	2.450E 03
8	03	=	01D	1.000E 00	0.000E-01
9	03	=	0	4.200E-02	0.000E-01
10	01D	=	0	4.290E 10	-1.000E 02
11	01D	=	2 OH	6.520E 09	0.000E-01
12	03	=	H02	1.000E 02	9.400E 02
13	03	=	OH	3.000E 00	5.800E 02
14	N03	=	2 N02	2.810E 04	-2.500E 02
15	N03	=	N0 +	5.900E-01	1.231E 03
16	N03	=	N205	1.780E 03	6.000E 01
17	N205	=	2 HN03	3.800E-02	0.000E-01
18	N205	=	N03 +	3.120E 00	1.084E 04
19	N0	=	2 HN02	3.200E-07	0.000E-01
20	HN02	=	N0 +	1.500E-05	0.000E-01
21	HN02	=	N0 +	1.800E-01	0.000E-01
22	N02	=	HN03	1.630E 04	-5.600E 02
23	N0	=	HN02	9.770E 03	-4.270E 02
24	H02	=	OH +	1.230E 04	-2.400E 02
25	N0	=	2 N02	1.520E-04	-5.300E 02

TABLE 3-1. (continued).

Reaction Number	Mechanism			k ₂₉₈ (ppm ⁻¹ min ⁻¹)	Activation Energy (E/R)
26	H2O2	=	2 OH	1.000E 00	0.000E-01
27	OH	=	H2O2	2.520E 03	1.870E 02
28	OH	=	HNO2	9.770E 03	0.000E-01
29	OH	=	HNO3	1.920E 02	-7.780E 02
30	N03	=	0.85 N02 + 0.85 O + 0.15 N0	3.060E 01	0.000E-01
31	H02	=	H2O2	4.144E 03	-1.150E 03
32	H02	=	H2O2	4.360E 03	-5.800E 03
33	H02	=	N02	1.630E 03	-6.170E 02
34	PNA	=	H02 +	5.120E 00	1.042E 04
35	OH	=	H02	4.000E 02	0.000E-01
36	FORM	=	FROX	1.480E 01	0.000E-01
37	FORM	=	H02 +	1.500E 04	0.000E-01
38	FORM	=	2 H02 +	1.000E 00	0.000E-01
39	FORM	=	C0	1.000E 00	0.000E-01
40	FORM	=	OH +	2.370E 02	1.550E 03
41	FORM	=	HNO3 +	9.300E-01	0.000E-01
42	FROX	=	N02 +	1.040E 04	0.000E-01
43	FROX	=	FORM +	9.000E 01	0.000E-01
44	ALD2	=	C2O3 +	6.360E 02	9.860E 02
45	ALD2	=	C2O3	2.400E 04	-2.500E 02
46	ALD2	=	C2O3 +	3.700E 00	0.000E-01
47	ALD2	=	ME02 +	1.000E 00	0.000E-01
48	ALD2	=	H02 +	5.000E 00	0.000E-01
49	C2O3	=	N0 +	1.650E 04	-2.500E 02
50	C2O3	=	N02	9.000E 03	-2.500E 02

TABLE 3-1. (continued).

Reaction Number			Mechanism		k_{298} ($\text{ppm}^{-1}\text{min}^{-1}$)	Activation Energy (E/R)
51	PAN		C203 +	N02	2.220E-02	1.400E 04
52	ME02	+	MPNA		6.000E 03	-7.350E 02
53	MPNA		ME02 +	N02	9.200E 01	1.040E 04
54	ME02	+	ME0	N02	1.100E 04	-1.800E 02
55	ME0	+	MNIT		4.440E 04	-2.000E 02
56	ME0	+	FORM +	H02	1.920E 03	0.000E-01
57	ME0	+	MEN3		2.220E 04	0.000E-01
58	ME0		FORM +	H02	3.940E 05	1.313E 03
59	MEN3	+	FORM +	N02	2.220E 03	3.600E 02
60	MNIT	+	FORM +	N0	2.370E 03	3.400E 02
61	MNIT		ME0 +	N0	3.000E-01	0.000E-01
62	ME02	+	0.7 ME0 + 0.65 FORM		5.030E 02	-2.200E 02
63	ME02	+	ME0 +	ME02	4.400E 03	0.000E-01
64	C203	+	2 ME02		3.700E 03	0.000E-01
65	ME02	+			8.900E 03	-1.300E 03
66	C203	+			9.600E 03	0.000E-01
67	AONE		ME02 +	C203	4.000E-05	0.000E-01
68	AONE	+	X02 +	FORM + C203	5.800E 02	0.000E-01
69	GLY		1.79 CO + 0.21 FORM + 0.19 H02		7.500E-03	0.000E-01
70	GLY	+	H02 +	2 CO	1.500E 04	0.000E-01
71	MGLY		C203 +	H02 + CO	2.000E-02	0.000E-01
72	MGLY	+	X02 +	C203	2.600E 04	0.000E-01
73	OH		ME02		2.100E 01	0.000E-01
74	PAR	+	0.92 X02 + 0.79 R0R + 0.13 H02 + 0.13 ALD2 - 0.13 PAR + .067 X02N		1.150E 03	0.000E-01

TABLE 3-1. (concluded)

Reaction Number	Mechanism			k ₂₉₈ (ppm ⁻¹ min ⁻¹)	Activation Energy (E/R)
94	MCRG	+	NO	1.000E 04	0.000E-01
95	MCRG	+	NO2	1.000E 03	0.000E-01
96	MCRG	=		7.500E 03	0.000E-01
97	MCRG	+	FORM	3.000E 01	0.000E-01
98	MCRG	+	ALD2	3.000E 01	0.000E-01
99	TOL	+	OH	9.750E 03	0.000E-01
100	PHEN	+	NO3	1.400E 04	0.000E-01
101	BZA	+	OH	2.000E 04	0.000E-01
102	BZ02	+	NO2	2.500E 03	0.000E-01
103	BZ02	+	NO	3.700E 03	0.000E-01
104	PBZN			2.200E-02	1.400E 04
105	BZA			4.000E-03	0.000E-01
106	PHO	+	NO2	2.000E 04	0.000E-01
107	XYL	+	OH	3.600E 04	0.000E-01
108	TLA	+	OH	2.000E 04	0.000E-01
109	X02	+	H02	5.000E 03	-1.300E 01
110	OH			8.800E 01	0.000E-01
111	X02N	+	NO	1.000E 03	0.000E-01
112	X02	+	C203	2.400E 03	0.000E-01
113	NR			1.000E 00	0.000E-01

TABLE 3-2. OZIPM-3 Listing of the CALL Mechanism.

Reaction Number	Mechanism			k_{298} ($\text{ppm}^{-1}\text{min}^{-1}$)	Activation Energy (E/R)
1	N02	=	N0 +	1.000E 00	0.000E-01
2	0	=	03	4.650E 06	-1.282E 03
3	0	=	N02	1.370E 04	0.000E-01
4	0	=	N02 +	3.300E 03	-8.940E 02
5	N0	=	N03	2.680E 01	1.370E 03
6	N02	=	N02	4.520E-02	2.450E 03
7	N0	=	03	2.750E 04	-2.520E 02
8	N0	=	N03	1.430E-04	-5.290E 02
9	N02	=	2 N02	1.710E 03	-2.730E 02
10	N205	=	N205	2.080E 00	1.138E 04
11	N205	=	N02 +	3.000E-02	0.000E-01
12	N02	=	2 HN03	5.980E-01	1.229E 03
13	N03	=	N0 +	1.000E 00	0.000E-01
14	N03	=	N0	1.000E 00	0.000E-01
15	03	=	N02 +	1.000E 00	0.000E-01
16	03	=	0	1.000E 00	0.000E-01
17	0*SD	=	0*SD	1.000E 00	0.000E-01
18	0*SD	=	2 OH	6.540E 09	0.000E-01
19	N0	=	0	4.320E 10	0.000E-01
20	HN0	=	HN0	9.750E 03	-8.330E 02
21	N02	=	N0 +	1.000E 00	0.000E-01
22	N02	=	OH	1.170E-04	0.000E-01
23	HN03	=	HN0 -	1.680E 04	-7.370E 02
24	CO	=	N03	1.890E 02	-7.780E 02
25	03	=	H02	3.220E 02	0.000E-01
			OH +	1.000E 02	9.420E 02
			N02 + HN03		

TABLE 3-2. (continued).

Reaction Number	Mechanism				k ₂₉₈ (ppm ⁻ⁿ min ⁻¹)		Activation Energy (E/R)
51	ALD2 +	OH	=	MC03 +	RC03	H02 +	2.360E 04
52	ALD2		=	C0 +	HCHO		1.000E 00
53	ALD2 +	N03	=	HN03 +	MC03	RC03	3.690E 00
54	MC03 +	N0	=	N02 +	HCHO	R02R +	1.140E 04
55	MC03 +	N02	=	PAN			7.570E 03
56	MC03 +	H02	=	ROOH	HCHO		4.430E 03
57	MC03 +	R02	=	0.5 H02 +	HCHO	R02	4.430E 03
58	MC03 +	RC03	=	H02 +	HCHO	RC03	3.690E 03
59	PAN		=	MC03 +	N02	RC03	2.210E-02
60	RCHO +	OH	=	RC03 +	PC03		2.930E 04
61	RCHO		=	ALD2 +	H02	C0 +	1.000E 00
62	RCHO +	N03	=	HN03 +	PC03	RC03	3.690E 00
63	PC03 +	N0	=	N02 +	ALD2	R02R +	1.140E 04
64	PC03 +	N02	=	PPN			7.570E 03
65	PC03 +	H02	=	ROOH	ALD2		4.430E 03
66	PC03 +	R02	=	0.5 H02 +	ALD2	R02	4.430E 03
67	PC03 +	RC03	=	H02 +	ALD2	RC03	3.690E 03
68	PPN		=	PC03 +	N02	RC03	2.210E-02
69	ACET		=	MC03 +	HCHO	RC03 +	1.000E 00
70	ACET +	OH	=	MGLY +	R02	R02	3.390E 02
71	MEK		=	MC03 +	ALD2	RC03 +	1.000E 00
					R02		

TABLE 3-2. (continued).

Reaction Number	Mechanism											k ₂₉₈ (ppm·n _m l·n ⁻¹)	Activation Energy (E/R)
72	MEK	+	OH	=	1.5 R02R	+	1.5 R02	+	0.5 MC03	+	0.5 ALD2	1.460E 03	7.450E 02
73	GLYX			=		+	0.5 HCHO	+	0.5 PC03	+	RC03		
74	GLYX	+	OH	=	0.13 HCHO	+	1.87 C0					1.000E 00	0.000E-01
75	GLYX	+	N03	=	0.63 H02	+	1.26 C0	+	0.37 GC03	+	0.37 RC03	1.700E 04	0.000E-01
				=	HN03	+	0.63 H02	+	1.26 C0	+	0.37 GC03	8.880E-01	2.058E 03
76	GC03	+	N02	=	GPAN							7.570E 03	-1.800E 02
77	GC03	+	N0	=	N02	+	H02	+	C0			1.140E 04	-1.800E 02
78	GPAN			=	GC03	+	N02	+	RC03			2.210E-02	1.354E 04
79	GC03	+	H02	=	ROOH	+	C0					4.430E 03	0.000E-01
80	GC03	+	R02	=	0.5 H02	+	C0	+	R02			4.430E 03	0.000E-01
81	GC03	+	RC03	=	H02	+	C0	+	RC03			3.690E 03	0.000E-01
82	MGLY			=	MC03	+	H02	+	C0	+	RC03	1.000E 00	0.000E-01
83	MGLY	+	OH	=	MC03	+	C0	+	RC03			2.510E 04	0.000E-01
84	MGLY	+	N03	=	HN03	+	MC03	+	C0	+	RC03	3.690E 00	1.427E 03
85	ALK4	+	OH	=	0.19 HCHO	+	0.31 ALD2	+	0.17 RCHO	+	0.34 ACET	4.760E 03	3.530E 02
86	ALK7	+	OH	=	.02 HCHO	+	.03 ALD2	+	0.25 RCHO	+	0.36 ACET	9.080E 03	2.890E 02
87	ALKN	+	OH	=	N02	+	0.15 MEK	+	1.5 RCHO	+	0.48 ALD2	2.980E 03	7.110E 02
				=		+	0.16 HCHO	+	1.39 R202	+	1.39 R02		
88	R02N	+	N0	=	ALKN							1.140E 04	-1.800E 02
89	R02N	+	H02	=	ROOH	+	MEK					4.430E 05	0.000E-01
90	R02N	+	R02	=	R02	+	0.5 H02	+	MEK			1.480E 00	0.000E-01
91	R02N	+	RC03	=	RC03	+	0.5 H02	+	MEK			4.430E 03	0.000E-01

TABLE 3-2. (continued).

Reaction Number	Mechanism			k ₂₉₈ (ppm ⁻¹ min ⁻¹)	Activation Energy (E/R)
92	R202 +	NO	=	1.140E 04	-1.800E 02
93	R202 +	H02	=	4.430E 03	0.000E-01
94	R202 +	R02	=	1.480E 00	0.000E-01
95	R202 +	RC03	=	4.430E 03	0.000E-01
96	R02R +	NO	=	1.140E 04	-1.800E 02
97	R02R +	H02	=	4.430E 03	0.000E-01
98	R02R +	R02	=	1.480E 00	0.000E-01
99	R02R +	RC03	=	4.430E 03	0.000E-01
100	ETHE +	OH	=	1.260E 04	-4.110E 02
101	ETHE +	O3	=	2.570E-03	2.634E 03
102	ETHE +	O	=	1.080E 03	7.920E 02
103	ETHE +	NO3	=	1.610E-01	2.925E 03
104	PRPE +	OH	=	3.890E 04	-5.040E 02
105	PRPE +	O3	=	1.670E-02	2.105E 03
106	PRPE +	O	=	5.880E 03	3.240E 02
107	PRPE +	NO3	=	1.120E 01	1.935E 03
108	TBUT +	OH	=	9.420E 04	-5.490E 02
109	TBUT +	O3	=	2.960E-01	1.137E 03
110	TBUT +	O	=	3.450E 04	-1.000E 01
111	TBUT +	NO3	=	5.610E 02	9.750E 02

TABLE 3-2. (concluded)

Reaction Number	Mechanism													k ₂₉₈ (ppm ⁻¹ min ⁻¹)	Activation Energy (E/R)		
112	TOLU	+	OH	=	0.16	CRES	+	0.16	H02	+	0.84	R02R	+	0.4	DIAL	9.080E 03	-3.200E 02
113	DIAL	+	OH	=		PC03	+		0.84	R02	+	0.144	MGLY	+	0.114	GLYX	4.430E 04
114	DIAL			=		H02	+		CO						RC03	1.000E 00	0.000E-01
115	XYLE	+	OH	=	0.17	CRES	+	0.17	H02	+	0.83	R02R	+	0.83	R02	RC03	3.620E 04
							+	0.65	DIAL	+	0.316	MGLY	+	.095	GLYX		-1.160E 02
116	TMBZ	+	OH	=	0.17	CRES	+	0.17	H02	+	0.83	R02R	+	0.83	R02		9.160E 04
							+	0.49	DIAL	+	0.86	MGLY					0.000E-01
117	CRES	+	OH	=	0.2	MGLY	+	0.15	R02P	+	0.85	R02R	+		R02		5.910E 04
118	R02P	+	NO	=		NPHE											1.140E 04
119	R02P	+	H02	=		ROOH											4.430E 03
120	R02P	+	R02	=	0.5	H02	+			R02							1.480E 00
121	R02P	+	RC03	=	0.5	H02	+			RC03							4.430E 03
122	CRES	+	NO3	=		HNO3	+			BZO							3.250E 04
123	BZO	+	NO2	=		NPHE											2.220E 04
124	BZO	+	H02	=		PHEN											4.430E 03
125	BZO			=		PHEN											6.000E-02
126	PHEN	+	OH	=	0.2	MGLY	+	0.15	R02P	+	0.85	R02R	+		R02		4.140E 04
127	PHEN	+	NO3	=		HNO3	+		BZO								5.620E 03
128	NPHE	+	NO3	=		HNO3	+		BZN2								5.620E 03
129	BZN2	+	NO2	=													2.220E 04
130	BZN2	+	H02	=		NPHE											4.430E 03
131	BZN2			=		NPHE											6.000E-02
132	NRHC			=		NRHC											6.000E 01

calculating future conditions based on present data. Once a future scenario is established, it is relatively simple to assess the effects of parametric changes and their impacts within that scenario. In this study, we feel that the mere resimulation of a present-day scenario using different photolysis rates or temperature values will not provide a reasonable enough estimate of anticipated future urban conditions because mandated control requirements must necessarily alter present conditions. Since the EKMA procedure is often used to determine the amount of NMOC reduction that will ideally be implemented in the future, we utilized this direct link with the regulatory process to determine more realistic future scenarios. Therefore, the present-day base-case data sets were implemented in OZIPM-3, and standard EKMA calculations were performed to formulate scenarios of future attainment in each city based on the alleviation of current smog scenarios. We felt that this approach would provide a much better estimate of future base-case scenarios with which to assess unanticipated (in the EKMA) perturbations due to changes in the two variables (temperature and ultraviolet radiation) of interest in this study. Of course, this protocol assumes "ideal" performance in the EKMA calculation method and an "ideal" response of an urban atmosphere to EKMA-derived emission controls. As we describe next, errors in the EKMA calculation method can be minimized by selective application of only the best predictions of present-day scenarios.

The principal strength of the EKMA procedure is its ability to compensate for non-ideal simulation of the measured ozone maximum concentration using the set of design conditions available for a specific day. This compensation is based on the expectation that the OZIPM photochemical mechanism will accurately reproduce the nonlinear NMOC, NO_x , and O_3 relationships in oxidant chemistry. In the current investigation, however, we actually altered the chemical mechanism between the simulation of present and future conditions by changing some future reaction rates through increases in temperature and ultraviolet irradiance. This is a situation that the EKMA procedure was not designed for. We therefore imposed additional constraints on our study that are not included in typical SIP calculations. One key constraint is that the simulated ozone value and the design (measured) concentration should not vary excessively. That is, we require a good fit between simulated ozone and measured ozone for the base-case simulation. In this way, the EKMA program is not required to compensate for a poor fit, but only to calculate the ratio of NMOC reduction needed to "ideally" produce 0.12 ppm ozone. We use such EKMA calculations to derive conditions of anticipated future NAAQS compliance for ozone. With these scenarios, which we denote as future base cases, we assessed the unanticipated impacts of changes to surface temperature and ultraviolet irradiance.

The overall investigation protocol is depicted in Figure 3-1 for one of the possible test cities. As shown, the number of simulations for each city was reduced depending on the goodness-of-fit between measured and simulated hourly maximum ozone concentrations for present base-case simulations (all base-case runs were simulated with measured or calculated temperature data and j-values for an ozone column of 0.300 cm-atm). EKMA calculations were then performed to determine the "ideal" NAAQS compliance conditions for each base-case data set. Occasionally, a few of these data sets provided wildly variable EKMA results and were deemed unusable. In addition, because some input data were rather uncertain, a few cities had poor base-case simulations. All simulations from Chicago and Boston were excluded from our base case pool. From the EKMA results, a future base-case data set (still with of normal temperature and ozone column conditions) was derived and simulated to verify that those conditions produced ozone at the level of the NAAQS. Then, using this future base case as the "ideal" anticipated result of prescribed NMOC reductions, we were able to predict the extent of the photochemical changes caused by increased temperature and ultraviolet irradiance. This was done by the incremental increase of these values and the analysis of resulting changes in the concentrations of ozone and other chemical species.

As described in Section 1, the measured (or calculated) temperature distribution specific to each test day was used for all the base-case simulations. In addition, since ozone column density data were not available for these cities, we used a value of 0.300 cm-atm (300 DU) as the base-case overhead ozone column density when calculating diurnally varying j-values. Perturbations to these two parameters were made by simply adding 2 and 5 K to the base-case temperatures, and by calculating j-values for overhead ozone columns of 0.250 and 0.200 cm-atm. The j-values were determined for an altitude 640 m above the surface elevation of each city using monthly average surface albedoes for each location (Iqbal, 1983). The temperature and ozone column density changes were made independently, and in combination, providing 9 future scenarios (including the future base case) for each data set.

INPUT DATA

Our initial, single-day modeling data set consisted of atmospheric measurements from 45 days in 10 cities. There were actually 57 initial base-case simulations because some days were modeled with a multiple number of trajectories. Table 3-3 provides a list of the cities studied, along with the number of days and trajectory data sets initially simulated. The elevation, location, regional albedo, temperature, and mixing height data are given in Appendix A for each date and city in these simulations.

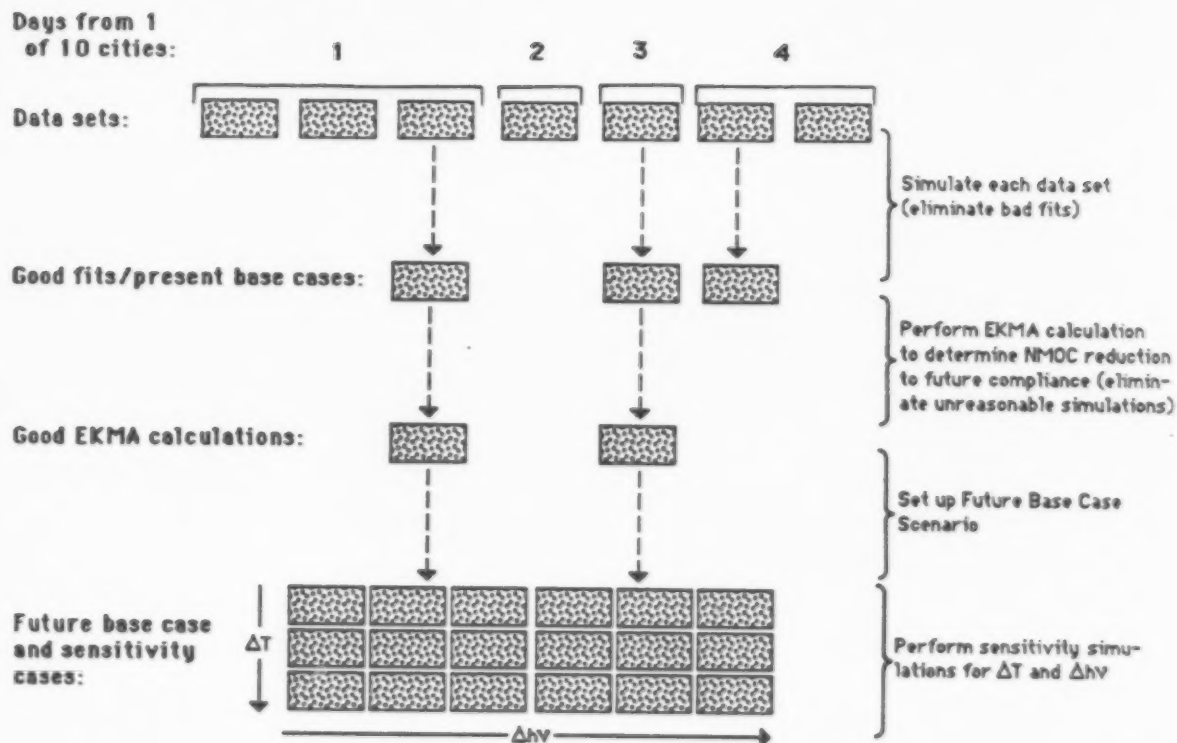


FIGURE 3-1. Single-day urban modeling data-set selection process protocol.

Table 3-3. Initial single-day data sets in the OZIPM/EKMA investigation.

<u>City</u>	<u>Number of Days</u>	<u>Number of Trajectories</u>
Chicago, IL	3	3
Los Angeles, CA	1	1
Boston, MA	7	7
Nashville, TN	6	9
New York, NY	1	2
Philadelphia, PA	6	7
Phoenix, AZ	4	5
Seattle, WA	3	8
Tulsa, OK	9	10
Washington, DC	<u>5</u>	<u>5</u>
TOTAL	45	57

Individual NMOC, NO_x , and design O_3 values are discussed later. The range of different city-specific input values in the test data sets is large, but the effect of individual differences is not always discernable because these changes are not isolated. In some particular cases, such as in the multi-day tests, we have altered some values to directly address individual parametric variations. However, in the single-day tests these values were unchanged. Two important parameters that vary in the single-day base-case data are the temperature and mixing height values (see Appendix A). In most data sets, the base-case temperatures vary diurnally from about 298 K to 305 K. Only in the case of Los Angeles, which has a 24-hour temperature field, does a more significant variation occur. As noted in Appendix A, the Los Angeles temperature profile extends from 294 K (at night) to 317 K. It is difficult to judge the effect of this change among different base-case simulations because Los Angeles also has one of the lowest mixing height profiles. It is possible to discern the temperature effect in the future simulations, however, since that parameter is individually varied.

Mixing height profiles appear to cover the range of variability expected for different cities throughout the United States. Diurnal changes on the west coast are generally small. For instance, the Los Angeles data varies from about 80 to 540 m, while the variation in Seattle could be as small as 250 to 670 m. This variation in mixing depth by a factor of less than 3, along with other conditions discussed next, creates a unique test set for Seattle. The smaller mixing height changes on the west coast can be compared to factors between 12 and 14 for some Phoenix, Tulsa, and Washington days. The remaining mixing height profiles for individual days fit between these data toward the higher values.

The photolysis rate ratios to j_{NO_2} that were used in the simulations are given in Appendix B for ozone [$\text{to O}(^1\text{D})$], formaldehyde, acetaldehyde, and hydrogen peroxide. These values are shown as a function of zenith angle and overhead ozone column. It can be seen from comparison of these values for different cities that no significant variation occurs in the zenith-angle dependency since regional albedo and elevation do not differ significantly throughout our set of test cities. On the other hand, because the latitude of a city affects the diurnal solar elevation function, areas located closer to the tropics will have lower zenith angles, and therefore, higher j -values for a given time of day. In this study, Seattle is located farthest north and Los Angeles and Phoenix are at the lowest latitudes. Figure 3-2 shows the zenith angle functions calculated for Seattle and Los Angeles for 1 August. The functions are slightly offset because of the differing longitudes of the cities, but the latitudinal differences translate into about a 13.7 degree variation in solar elevation at local solar noon. Figure 3-3 shows the j_{O_3} values calculated for

Zenith Angle Comparison

Los Angeles, CA vs. Seattle, WA

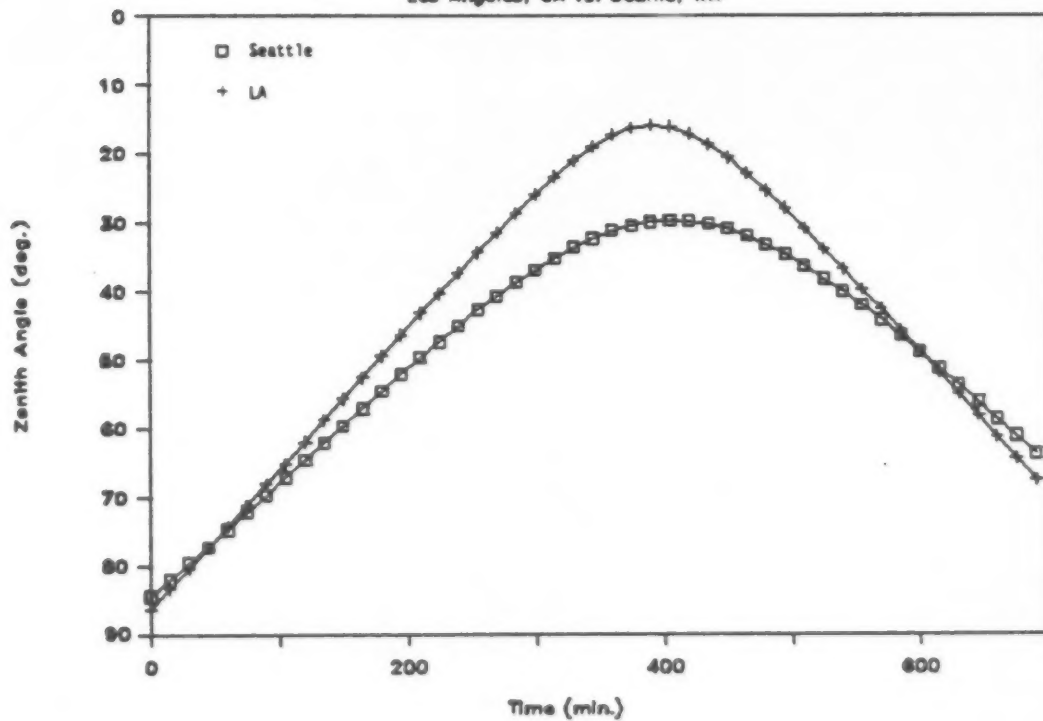


FIGURE 3-2. Calculated zenith angles for Seattle, Washington and Los Angeles, California for 1 August.

Comparison of Calculated j -Values

Los Angeles, CA vs. Seattle, WA

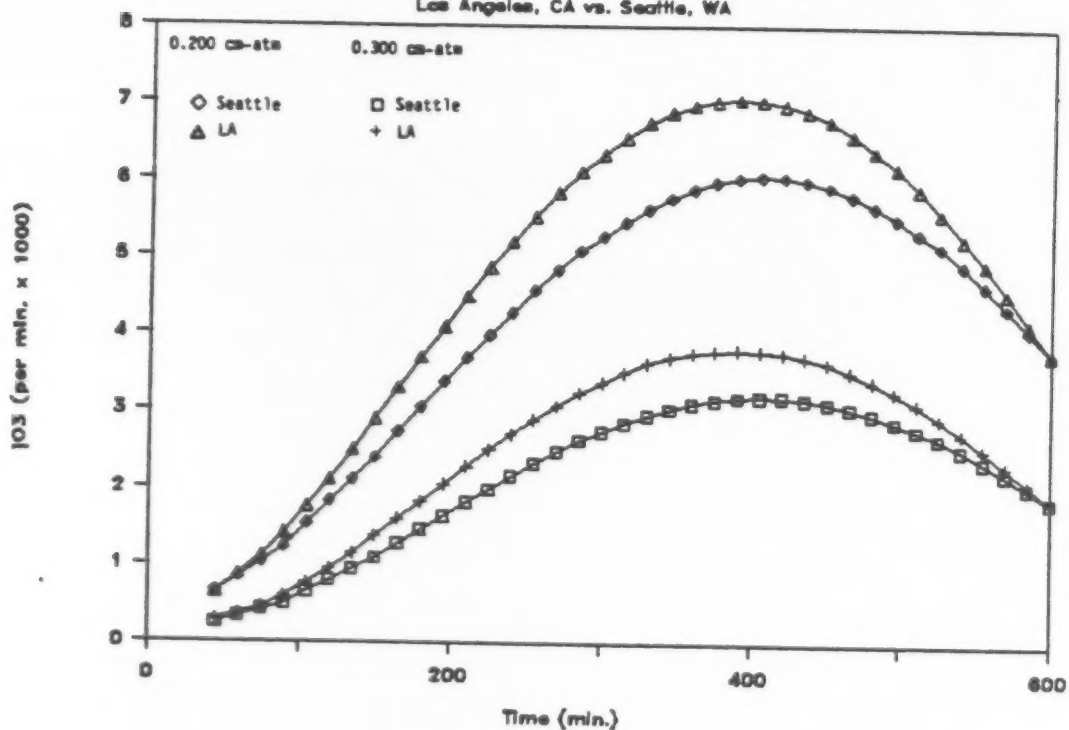


FIGURE 3-3. Calculated j_{03} values for Seattle, Washington and Los Angeles, California for 1 August at 0.300 and 0.200 cm-atm overhead ozone column.

both cities on that date as a function of time and overhead ozone column. Integrating over the four-hour period centered on local solar noon, we calculate the average Seattle j_{O_3} value to be $3.17 \times 10^{-3} \text{ min}^{-1}$ at a 0.300 cm-atm overhead ozone column, and that of Los Angeles to be $3.76 \times 10^{-3} \text{ min}^{-1}$. This represents a 20 percent difference in photolysis rates at 0.300 cm-atm, with slightly less difference for the 0.200 cm-atm ozone column calculations.

These variations demonstrate a localized difference in energy input between two urban areas. Assuming all other factors are equal, areas with additional radiant energy input would most likely be required to implement more NMOC emission controls to attain the same air quality because that additional energy input would make their urban atmospheric mixture of oxidant precursors more reactive. Conversely, northern areas with lower energy input might not require extra controls because the energy input is low enough to render the photochemical production of oxidants less efficient. However, as we discuss next, since these precursors are not controlled, they will continue to exist downwind of the city. As conditions change to future conditions of enhanced ultraviolet irradiance and temperature, these uncontrolled precursors might achieve significantly greater oxidant-forming potential within the city. Hence, one effect of future increased ultraviolet irradiance is somewhat like moving a city to lower latitudes, where conditions could produce more oxidant and oxidized products.

Finally, since the city-specific data sets presented in the appendixes span a wide range of urban oxidant production capacities, we have consolidated the following discussion by creating three general group classifications:

Group 1: High ozone NAAQS exceedence days. In this group we include all days with design values greater than 0.17 ppm. There are ten such days in the 45 days simulated. These data sets are from Los Angeles, Chicago, New York, Boston, Philadelphia, and Washington, representing oxidant production episodes in regions where severe ozone exceedences are common.

Group 2: Less extreme nonattainment days, often representing cities that require moderate control (30 to 50 percent) of organic precursors to achieve the ozone NAAQS. Hourly maximum ozone concentrations are between 0.17 and 0.14 ppm in this group. Local meteorological conditions can influence the magnitude of the ozone production in many of these cases.

Group 3: Days that are nearly in compliance with the NAAQS for ozone. These data sets provide future sensitivity tests with current ozone production at 0.13 ppm or below. The data are scattered between a few test cities, including Boston, Nashville, and Tulsa.

We have used these groupings because common group characteristics facilitate later discussion of chemical dynamics. Although these data could be considered typical of each individual city's ozone formation profile, we will usually name specific cities only to identify the source of input data for an example data set. One notable exception in the following discussion concerns the two data sets chosen from the Seattle data. As with many data sets collected for use in the 1982 SIP process in smaller cities, some measurements needed for OZIPM input parameters appear to be rather uncertain. In this case, we refer to both the precursor concentrations (which appear to be rather high) and the morning mixing height (which may have been less than the 250-m values used in the SIP calculations). The calculated results for those days do not easily fit into any of the grouping schemes. However, their results do demonstrate some important atmospheric processes; so, though they are uncertain, we discuss the conditions and predictions from those two tests to demonstrate certain aspects of chemical dynamics. Therefore, our discussion focuses on the three general groups, and a fourth test based on the Seattle data (denoted as Group 4 in the following discussion). We feel that this grouping scheme is as specific as the current data will allow. We stress that though it is based on data from one city, even the Seattle data should be considered a general test case since a much larger and better defined set of city-specific measurements must be considered before the unique characteristics of any individual city can actually be discussed.

In addition to the single-day tests, two multi-day data sets were used to investigate the conditional variation of ozone and oxidized species with potential future changes in surface temperature and ozone column density previously described. One multi-day scenario was chosen to represent an urban area in conditions of compliance with the ozone NAAQS. The second was to represent a non-compliance day. For the non-compliance tests, we utilized a two-day data set from Los Angeles for 26-27 June 1974. Since the first day was used as our only Los Angeles simulation day, we had already performed EKMA calculations and derived future base-case conditions for that day (see Section 4). Therefore, we used those input data to begin our multi-day tests. On the other hand, because we had no data sets for NAAQS attainment conditions (since the sources of our data are SIP simulations of non-compliance days), we selected one of the lower ozone production Phoenix days (5 July 1980) and altered the data slightly to produce conditions of approximately 0.1 ppm maximum predicted hourly ozone concentrations. The alterations consisted of utilizing the Phoenix mixing height data from the day with the largest change (dilution) and

slightly lowering initial conditions and emissions. Since this day was already nearly in compliance and these changes were rather small, we felt that these initial conditions were realistic.

Finally, two sets of simulations were performed using the alternate chemical mechanism. We chose the (original) 5 July 1980 Phoenix test case to represent Group 2, and the 13 July 1979 Philadelphia data to test the more reactive Group 1. Except for mechanism changes, no alterations were made to the original simulation input conditions.

RESULTS

In this section we first discuss the single-day simulation results for both the base-case simulations and the future case results. Because the multi-day simulations and the tests performed with the alternate mechanism are based on the single-day simulations, only the future results will be discussed here.

As noted in the protocol section, each single-day data set was simulated with the best base-case information obtainable to ascertain the goodness-of-fit of maximum hourly ozone concentration with those data. The NMOC, NO_x , NMOC/ NO_x ratios, and design O_3 concentrations for each of the 57 data sets are presented in Table 3-4, along with the predicted maximum hourly ozone concentrations. From these simulations, we selected one to four data sets from each city, depending on the similarity between predicted maximum hourly ozone concentrations and measured values.

After the set of input files was thus reduced, we performed EKMA calculations to determine the potential future conditions of hydrocarbon control resulting in attainment of the ozone NAAQS. In a few cases, the method would not converge to an EKMA solution. In some other cases, the isopleth shape was such that calculation of the necessary hydrocarbon changes could not start from or near the original NMOC and NO_x concentrations on the NMHC/ NO_x line. Both types of data were set aside, leaving 15 future base-case data sets with good base-case fits and reasonable EKMA calculations starting from very near the original base-case NMOC and NO_x concentrations. These data sets, which are based on city-specific information from 8 different cities, are listed in Table 3-5 by the general categories discussed earlier. We feel that this process has eliminated much of the most questionable data in an unbiased manner. The set of test data presented in Table 3-5 should provide a basis for focusing on the photochemical dynamic aspects of global climate change as it relates to urban atmospheres. On the other hand, we repeat that these study data are not extensive enough to allow conclusions regarding individual cities; hence, the following discussion focuses on the generalized groups.

Table 3-4. Design values and model results for BASE CASE simulations.

<u>Date¹</u>	<u>Design Values (ppm)</u>				<u>Simulated</u>	
	<u>NMOC</u>	<u>NO_x</u>	<u>Ratio</u>	<u>O₃</u>	<u>O₃</u>	<u>Pct.</u>
BOSTON:						
30 May 1978	0.312	0.034	9.4	0.240	0.143	-40.4
21 July 1978	0.231	0.033	7.0	0.150	0.109	-27.3
13 August 1978	0.310	0.034	9.4	0.125	0.140	12.0
15 August 1978	0.312	0.034	9.4	0.160	0.147	- 8.1
16 August 1978	0.231	0.033	7.0	0.140	0.113	-19.3
29 June 1979	0.191	0.023	8.3	0.125	0.148	18.4
10 July 1979	0.191	0.023	8.3	0.160	0.111	-30.6
CHICAGO:						
10 July 1979	1.050	0.157	6.7	0.174	0.139	-20.1
11 July 1979	0.375	0.056	6.7	0.177	0.144	-18.6
26 August 1980	0.875	0.131	6.7	0.170	0.131	-22.9
LOS ANGELES:²						
26 June 1974	0.168	0.027	6.2	0.490	0.447	- 8.8
NASHVILLE:						
2 July 1980	0.256	0.054	4.7	0.130	0.087	-33.1
25 July 1980-1	0.168	0.036	4.7	0.130	0.085	-34.6
25 July 1980-2	0.196	0.043	4.6	0.130	0.097	-25.4
1 August 1980-1	0.176	0.037	4.8	0.130	0.076	-41.5
1 August 1980-2	0.203	0.044	4.6	0.130	0.089	-31.5
10 August 1980-1	0.412	0.088	4.7	0.130	0.121	- 6.9
10 August 1980-2	0.456	0.098	4.7	0.130	0.135	3.8
11 September 1981	0.336	0.070	4.8	0.156	0.094	-39.7
12 September 1981	0.238	0.052	4.6	0.127	0.087	-31.5

Table 3-4. (continued).

<u>Date¹</u>	<u>Design Values (ppm)</u>				<u>Simulated</u>	
	<u>NMOC</u>	<u>NO_x</u>	<u>Ratio</u>	<u>O₃</u>	<u>O₃</u>	<u>Pct.</u>
NEW YORK:						
24 June 1980-1	2.03	0.122	16.6	0.253	0.226	-10.7
24 June 1980-2	2.03	0.122	16.6	0.234	0.235	0.4
PHILADELPHIA:						
13 July 1979	0.916	0.125	7.3	0.200	0.237	18.5
19 July 1979	0.916	0.125	7.3	0.170	0.136	-20.0
24 June 1980	0.765	0.093	8.2	0.171	0.173	1.1
15 June 1981	0.916	0.125	7.3	0.206	0.171	-17.0
16 June 1981	0.883	0.148	6.0	0.161	0.233	44.7
19 August 1982	0.916	0.125	7.3	0.157	0.144	- 8.3
27 June 1983-1	0.916	0.125	7.3	0.156	0.209	34.0
27 June 1983-2	0.916	0.125	7.3	0.150	0.163	8.7
PHOENIX:						
5 July 1984	0.397	0.026	15.3	0.140	0.143	2.1
29 August 1984	1.301	0.072	18.1	0.140	0.140	0.0
31 August 1984	1.004	0.094	10.7	0.130	0.133	2.3
14 September 1984-1	1.857	0.135	13.8	0.160	0.185	15.6
14 September 1984-2	1.857	0.135	13.8	0.140	0.164	17.1
SEATTLE:						
7 August 1981-1	1.620	0.30	5.4	0.14	0.134	- 4.3
7 August 1981-2	1.620	0.30	5.4	0.13	0.136	4.6
10 August 1981-1	1.458	0.27	5.4	0.14	0.149	6.4
10 August 1981-2	1.458	0.27	5.4	0.15	0.150	0.0
10 August 1981-3	1.458	0.27	5.4	0.13	0.149	14.6
11 August 1981-1	1.404	0.26	5.4	0.14	0.131	- 6.4
11 August 1981-2	1.404	0.26	5.4	0.15	0.129	-14.0
11 August 1981-3	1.404	0.26	5.4	0.13	0.132	1.5

Table 3-4. (concluded).

<u>Date¹</u>	<u>Design Values (ppm)</u>				<u>Simulated</u>	
	<u>NMOC</u>	<u>NO_x</u>	<u>Ratio</u>	<u>O₃</u>	<u>O₃</u>	<u>Pct.</u>
TULSA:						
1 July 1981	1.589	0.0623	25.5	0.148	0.123	-16.9
16 July 1981-1	1.589	0.0623	25.5	0.157	0.110	-29.9
16 July 1981-2	1.589	0.0623	25.5	0.157	0.115	-26.8
6 August 1981	1.589	0.0623	25.5	0.148	0.115	-22.3
29 June 1982	1.589	0.0623	25.5	0.130	0.117	-10.0
6 August 1982	1.589	0.0623	25.5	0.128	0.115	-10.2
23 August 1982	1.589	0.0623	25.5	0.148	0.088	-40.5
26 July 1983	1.589	0.0623	25.5	0.138	0.112	-18.8
27 August 1983	1.589	0.0623	25.5	0.134	0.107	-20.1
28 August 1983	1.589	0.0623	25.5	0.131	0.106	-19.1
WASHINGTON:						
16 July 1980	0.75	0.116	6.5	0.16	0.040	-75.0
17 July 1980	0.76	0.076	10.0	0.20	0.112	-44.0
21 July 1980	0.82	0.080	10.3	0.14	0.136	- 2.9
7 August 1980	0.54	0.063	8.6	0.18	0.164	- 8.9
29 August 1980	1.16	0.150	7.7	0.14	0.112	-20.0

¹Hyphenated dates refer to different trajectories used on the same day.

²The Los Angeles simulation was a 1600 to 1600, 24 hour run; therefore, the NMOC and NO_x values are not 6-9 AM averages.

Table 3-5. Data Sets Used in Future Scenario Tests¹

City	Date	Design Values			Simulation		EKMA Control	
		NMOC	NO _x	HC/NO _x	O ₃	% Dif.		
GROUP 1:								
Los Angeles, CA	26 June 1974	0.168 ²	0.027 ²	6.2 ²	0.490	0.447	- 8.8	84
New York, NY	24 June 1980	2.03	0.122	16.6	0.234	0.235	0.4	77
Philadelphia, PA	13 July 1979	0.916	0.125	7.3	0.200	0.237	18.5	56
Washington, DC	7 August 1980	0.54	0.063	8.6	0.18	0.164	- 8.7	24
Philadelphia, PA	24 June 1980	0.765	0.093	8.2	0.171	0.173	1.2	28
GROUP 2:								
Phoenix, AZ	14 September 1984	1.857	0.135	13.8	0.16	0.185	15.6	47
Tulsa, OK	1 July 1981	1.589	0.062	25.5	0.148	0.123	-16.9	74
Washington, DC	21 July 1980	0.82	0.080	10.3	0.14	0.136	- 2.9	29
Phoenix, AZ	5 July 1984	0.397	0.026	15.3	0.14	0.143	2.1	34
GROUP 3:								
Nashville, TN	10 August 1980 (1) ³	0.412	0.088	4.7	0.13	0.121	- 6.9	50
Nashville, TN	10 August 1980 (2) ³	0.456	0.098	4.7	0.13	0.135	3.8	50
Phoenix, AZ	31 August 1984	1.004	0.094	10.7	0.13	0.133	2.3	18
Tulsa, OK	6 August 1982	1.589	0.062	25.5	0.128	0.115	-10.2	43
GROUP 4:								
Seattle, WA	11 August 1981	1.404	0.26	5.4	0.15	0.129	-14.0	8
Seattle, WA	7 August 1981	1.620	0.30	5.4	0.13	0.136	4.6	3

¹Significant figures in table as given in data sources.²Because the Los Angeles simulation was a 24-hour test, these values do not represent 6-9 AM NMOC and NO_x concentrations.³Two trajectories were modeled for this day.

As described in the protocol discussion, nine future case scenarios were performed for each set of future conditions. The future base case was formulated from the EKMA-determined conditions for future compliance with the ozone NAAQS. Perturbations due to either increases in temperature or ultraviolet irradiance (or both) were made to this future base case to derive eight other future climate change scenarios. The temperature was increased from the measured profiles by adding 2 or 5 K to each hourly data point, and the ultraviolet intensity was increased by changing calculated rate constants from their values at the base-case ozone column (0.300 cm-atm or 300 Dobson) to values determined at 0.250 and 0.200 cm-atm.

The maximum hourly ozone, hydrogen peroxide and PAN concentrations of the nine individual future scenario calculations for the 15 single-day test sets are tabulated in Tables 3-6 through 3-20. In this study we are particularly interested in changes in urban oxidant-formation potential; therefore, we also show the ozone and hydrogen peroxide results as bar charts following each table (Figures 3-4 through 3-18). The order of these results follows the listing of Table 3-5.

Two multi-day test sets were formulated from existing data--one representing ozone NAAQS attainment conditions and one representing non-attainment. The non-attainment set was derived from the 26-27 June 1974 episode in Los Angeles. We have already described the base-case results and EKMA calculations for the 26 June 1974 simulation of the first day of this episode. The future base-case conditions from the single-day scenario were used for the multi-day simulations. The other multi-day test set was for a situation of initial attainment of the ozone NAAQS. The input data for this test case were derived from available Phoenix data as described earlier. No EKMA calculations were necessary because of the compliance status for this test set, so future simulations were performed using the original base-case input values. The results from the future scenario tests for these two data sets are shown in Figures 3-19 and 3-20, and recorded in Tables 3-21 and 3-22.

As noted earlier, we performed complete analyses of two data sets with the CALL mechanism to verify that these results were not overly mechanism-specific. The 13 July 1979 Philadelphia data set was selected to represent a Group 1 test, and the 5 July 1984 Phoenix data was selected to represent Group 2. A complete reanalysis of each day, including base-case simulation, EKMA calculation, and the nine future scenario calculations were performed with the alternate mechanism. The results of the future scenarios are reported in Tables 3-23 and 3-24.

TABLE 3-6. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 26 June 1974, Los Angeles, California.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.112	0.113	0.114	--	0.9	1.8
250	0.126	0.129	0.131	12.5	15.2	17.0
200	0.157	0.162	0.165	40.2	44.6	47.3

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.01	0.01	0.01	--	0.0	0.0
250	0.01	0.01	0.01	0.0	0.0	0.0
200	0.03	0.04	0.05	200.0	300.0	400.0

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.71	0.57	0.40	--	-19.7	-43.7
250	0.75	0.60	0.42	5.6	-15.5	-40.9
200	0.96	0.81	0.59	35.2	14.1	-16.9

TABLE 3-7. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 24 June 1980, New York.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.125	0.130	0.138	--	4.0	10.4
250	0.150	0.157	0.167	20.0	25.6	33.6
200	0.165	0.170	0.178	32.0	36.0	42.4

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.05	0.06	0.08	--	20.0	60.0
250	0.43	0.58	0.84	760.0	1060.0	1580.0
200	3.08	3.31	3.60	6060.0	6520.0	7100.0

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.98	3.50	2.79	--	-12.1	-29.9
250	5.85	5.26	4.34	47.0	32.2	9.1
200	7.59	6.73	5.49	90.7	69.1	37.9

TABLE 3-8. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.118	0.122	0.129	--	3.4	9.3
250	0.142	0.146	0.152	20.3	23.7	28.8
200	0.153	0.157	0.162	29.7	33.1	37.3

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.07	0.09	0.13	--	28.6	85.7
250	0.86	0.99	1.19	1128.6	1314.3	1600.0
200	3.80	3.90	4.01	5328.6	5471.4	5628.6

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	2.06	1.80	1.44	--	-12.6	-30.1
250	3.29	2.84	2.23	59.7	37.9	8.3
200	4.13	3.54	2.73	100.5	71.8	32.5

TABLE 3-9. Maximum hourly concentrations and percentage changes for ozone, H₂O₂, and PAN for the future sensitivity tests for the simulation of 7 August 1980, Washington, DC.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.119	0.125	0.134	--	5.0	12.6
250	0.142	0.150	0.163	19.3	26.1	36.0
200	0.171	0.178	0.188	43.7	49.6	58.0

H₂O₂

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.03	0.04	0.05	--	33.3	66.7
250	0.13	0.19	0.32	333.3	533.3	966.7
200	1.53	1.82	2.24	5000.0	5966.7	7366.7

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.42	3.08	2.58	--	- 9.9	-24.6
250	5.00	4.63	4.04	4.6	35.4	18.1
200	7.64	6.87	5.76	123.4	100.9	68.4

TABLE 3-10. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 24 June 1980, Philadelphia, Pennsylvania.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.119	0.124	0.132	--	4.2	10.9
250	0.144	0.150	0.158	21.0	26.1	32.8
200	0.156	0.160	0.167	31.2	34.5	40.3

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.06	0.08	0.12	--	33.3	100.0
250	0.57	0.73	0.97	850.0	1116.7	1516.7
200	2.87	3.07	3.28	4683.3	5016.7	5366.7

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	2.50	2.18	1.76	--	- 12.8	- 29.6
250	3.86	3.40	2.74	54.4	36.0	9.6
200	5.11	4.46	3.60	104.4	78.4	44.0

TABLE 3-11. Maximum hourly concentrations and percentage changes for ozone, H₂O₂, and PAN for the future sensitivity tests for the simulation of 14 September 1974, Phoenix, Arizona.

OZONE

Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.120	0.124	0.129	--	3.3	7.5
250	0.129	0.132	0.136	7.5	10.0	13.3
200	0.133	0.136	0.139	10.8	13.3	15.8

H₂O₂

Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.52	0.60	0.72	--	15.4	38.5
250	1.38	1.47	1.60	165.4	182.7	207.7
200	2.86	2.92	2.99	450.0	461.5	475.0

PAN

Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	2.23	1.91	1.47	--	-14.4	-34.1
250	2.76	2.34	1.79	23.8	4.9	-19.7
200	3.24	2.75	2.08	45.3	23.3	- 6.7

TABLE 3-12. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 1 July 1981, Tulsa, Oklahoma.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.122	0.126	0.131	--	3.3	7.4
250	0.120	0.124	0.129	-1.6	1.6	5.7
200	0.115	0.119	0.124	-5.7	-2.5	1.6

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	2.87	2.95	3.07	--	2.8	7.0
250	4.19	4.25	4.32	46.0	48.1	50.5
200	5.83	5.87	5.90	103.1	104.5	105.6

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.92	3.46	2.79	--	-11.7	-28.8
250	4.24	3.79	3.13	8.2	- 3.3	-20.2
200	4.68	4.23	3.53	19.4	7.9	-10.0

TABLE 3-13. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 21 July 1980, Washington, DC.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.120	0.124	0.128	--	3.3	6.7
250	0.124	0.127	0.131	3.3	5.8	9.2
200	0.126	0.129	0.134	5.0	7.5	11.7

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.91	1.02	1.18	--	12.1	29.7
250	2.16	2.26	2.39	137.4	148.4	162.6
200	3.88	3.94	4.05	326.4	333.0	345.1

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.14	2.77	2.22	--	-11.7	-29.3
250	3.66	3.21	2.60	16.6	2.2	-17.2
200	4.31	3.83	3.14	37.3	22.0	0.0

TABLE 3-14. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona.

OZONE						
Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	0.119	0.122	0.125	--	2.5	5.0
250	0.121	0.124	0.127	1.7	4.2	6.7
200	0.121	0.124	0.127	1.7	4.2	6.7

H_2O_2						
Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	2.64	2.66	2.67	--	0.8	1.1
250	3.61	3.62	3.60	36.7	37.1	36.4
200	4.90	4.88	4.82	85.6	84.9	82.6

PAN						
Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	2.32	1.93	1.45	--	-16.8	-37.5
250	2.61	2.18	1.64	12.5	- 6.0	-29.3
200	2.92	2.46	1.87	25.9	6.0	-19.4

TABLE 3-15. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 1).

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.119	0.120	0.122	--	0.8	2.5
250	0.116	0.118	0.117	-2.5	-0.8	-1.7
200	0.111	0.112	0.112	-6.7	-5.9	-5.9

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.01	3.02	3.03	--	0.3	0.7
250	4.40	4.39	4.38	46.2	45.9	45.5
200	5.70	5.71	5.63	89.4	89.7	87.0

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	1.75	1.47	1.11	--	-16.0	-36.6
250	1.97	1.69	1.28	12.6	- 3.4	-26.9
200	2.30	1.96	1.52	31.4	12.0	-13.1

TABLE 3-16. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 2).

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.120	0.121	0.122	--	0.8	1.7
250	0.117	0.118	0.118	-2.5	-1.7	-1.7
200	0.113	0.114	0.114	-5.8	-5.0	-5.0

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.06	3.07	3.08	--	0.3	0.7
250	4.47	4.46	4.41	46.1	45.8	44.1
200	5.83	5.80	5.73	90.5	89.5	87.3

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	1.77	1.48	1.10	--	-16.4	-37.9
250	1.97	1.67	1.28	11.3	-5.7	-27.7
200	2.27	1.94	1.49	28.3	9.6	-15.8

TABLE 3-17. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 31 August 1984, Phoenix, Arizona.

OZONE						
Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	0.122	0.126	0.134	--	3.3	9.8
250	0.124	0.127	0.134	1.6	4.1	9.8
200	0.124	0.128	0.133	1.6	4.9	9.0

H_2O_2						
Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	1.29	1.39	1.61	--	7.8	24.8
250	2.15	2.22	2.43	66.7	72.1	88.4
200	3.36	3.45	3.57	160.5	167.4	176.7

PAN						
Change in Temp (K)	Concentration (ppb)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	4.12	3.71	3.11	--	-10.0	-24.5
250	4.65	4.22	3.54	12.9	2.4	-14.1
200	5.41	4.96	4.25	31.3	20.4	3.2

TABLE 3-18. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 6 August 1982, Tulsa, Oklahoma.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.122	0.126	0.131	--	3.3	7.4
250	0.118	0.122	0.127	-3.3	0.0	4.1
200	0.115	0.119	0.126	-5.7	-2.5	3.3

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	5.01	5.03	5.06	--	0.4	1.0
250	5.90	5.92	5.96	17.8	18.2	20.0
200	7.06	7.11	7.13	40.9	41.9	42.3

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	4.90	4.36	3.66	--	-11.0	-25.3
250	5.22	4.69	3.97	6.5	-4.3	-19.0
200	5.68	5.17	4.47	15.9	5.5	-8.8

TABLE 3-19. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 11 August 1981, Seattle, Washington.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.116	0.123	0.130	--	6.0	12.1
250	0.136	0.145	0.156	17.2	25.0	34.5
200	0.170	0.182	0.198	46.6	56.9	70.7

H_2O_2

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.00	0.00	0.00			
250	0.01	0.01	0.01			
200	0.01	0.02	0.03			

PAN

Change in Temp (K)	<u>Concentration (ppb)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.41	2.86	2.21	--	-16.1	-35.2
250	4.46	3.82	3.06	30.8	12.0	-10.3
200	6.53	5.70	4.84	91.5	67.2	41.9

TABLE 3-20. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 7 August 1981, Seattle, Washington.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.117	0.123	0.133	--	5.1	13.7
250	0.138	0.146	0.159	18.0	24.8	35.9
200	0.171	0.184	0.203	46.2	57.3	73.5

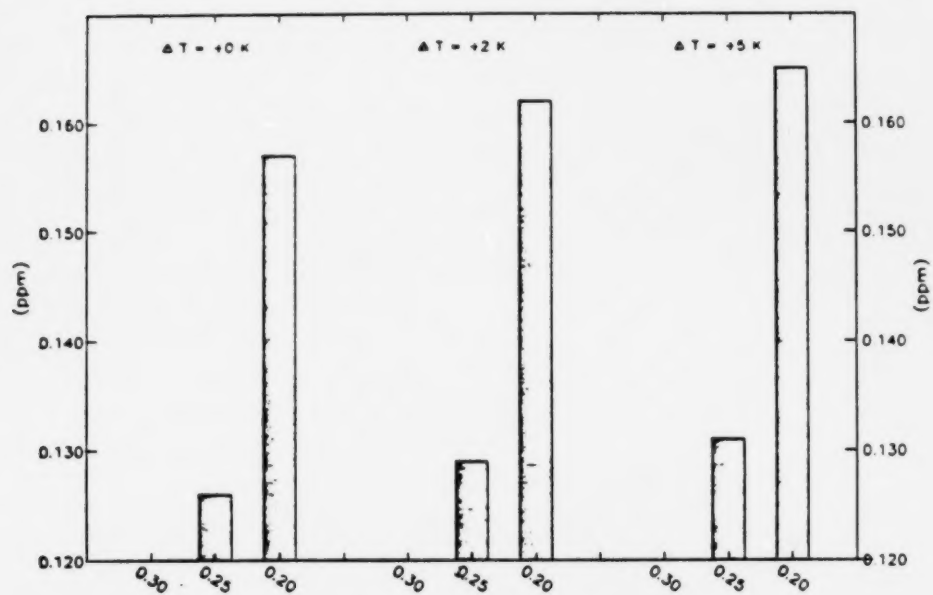
H_2O_2

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.01	0.01	0.01	--	0.0	0.0
250	0.01	0.01	0.02	0.0	0.0	100.0
200	0.03	0.04	0.06	200.0	300.0	500.0

PAN

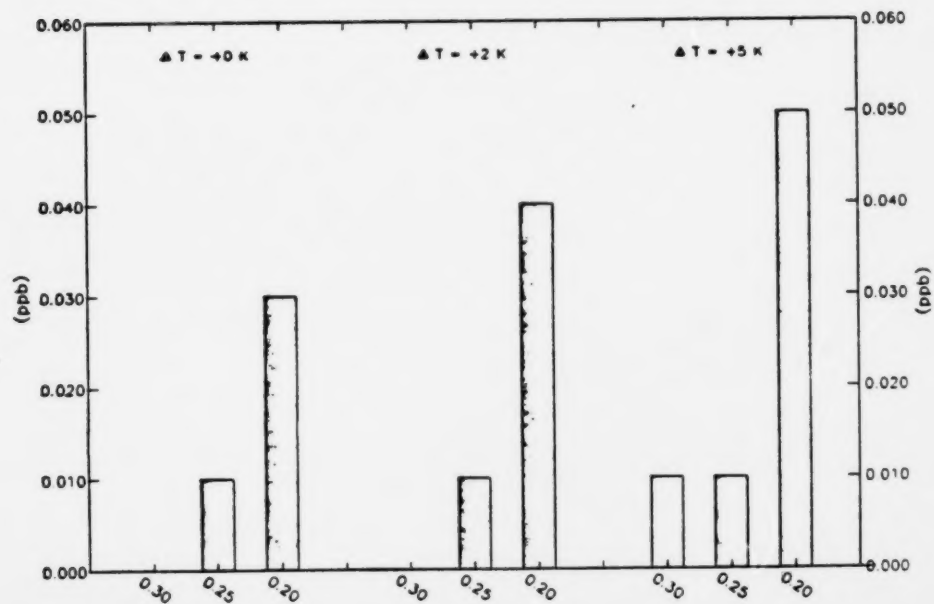
Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	4.12	3.60	2.89	--	-12.6	-29.9
250	5.44	4.86	4.02	32.0	18.0	- 2.4
200	7.93	7.34	6.48	92.5	78.2	57.3

OZONE



Los Angeles: June 26, 1974

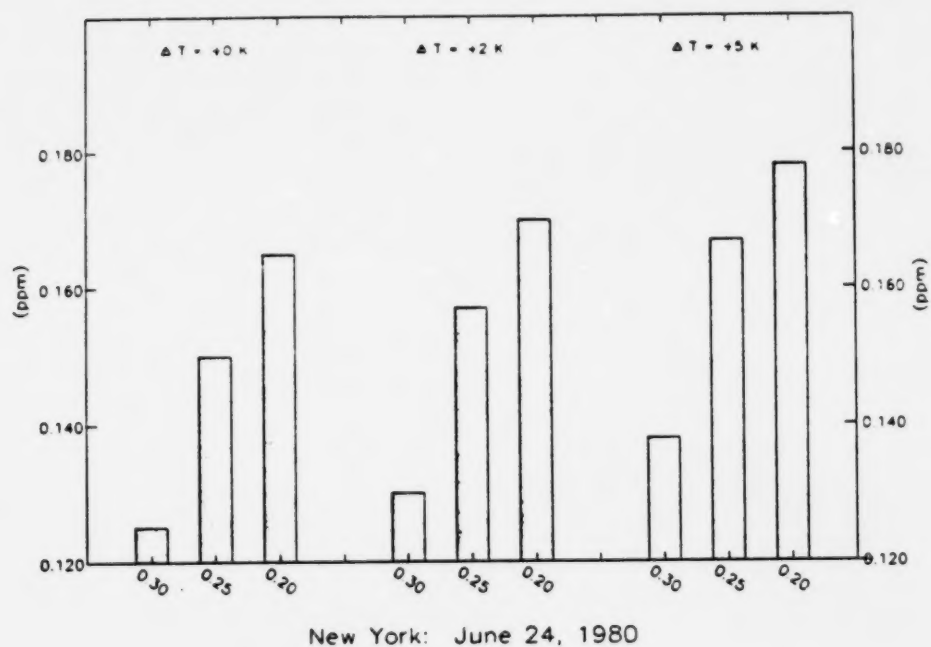
H2O2



Los Angeles: June 26, 1974

FIGURE 3-4. Results of OZIPM future sensitivity tests for the simulation of 26 June 1974, Los Angeles, California.

OZONE



H2O2

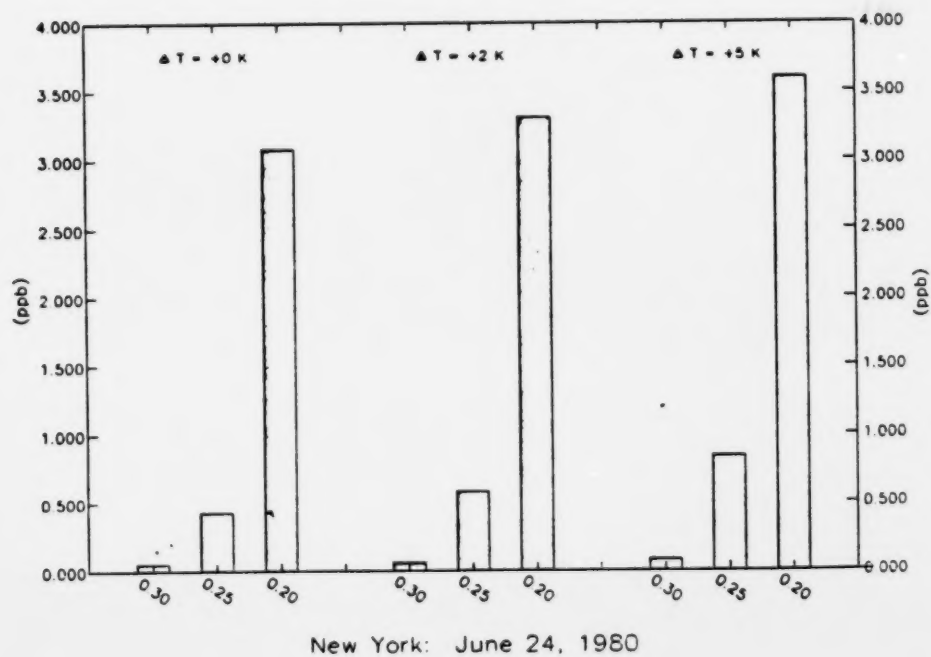
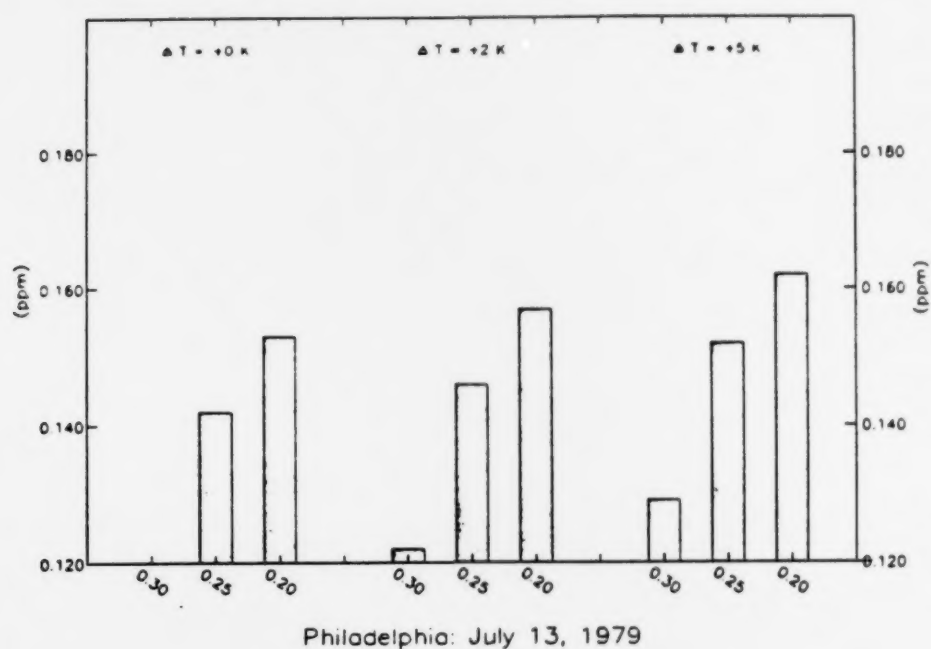


FIGURE 3-5. Results of OZIPM future sensitivity tests for the simulation of 24 June 1980, New York.

OZONE



H2O2

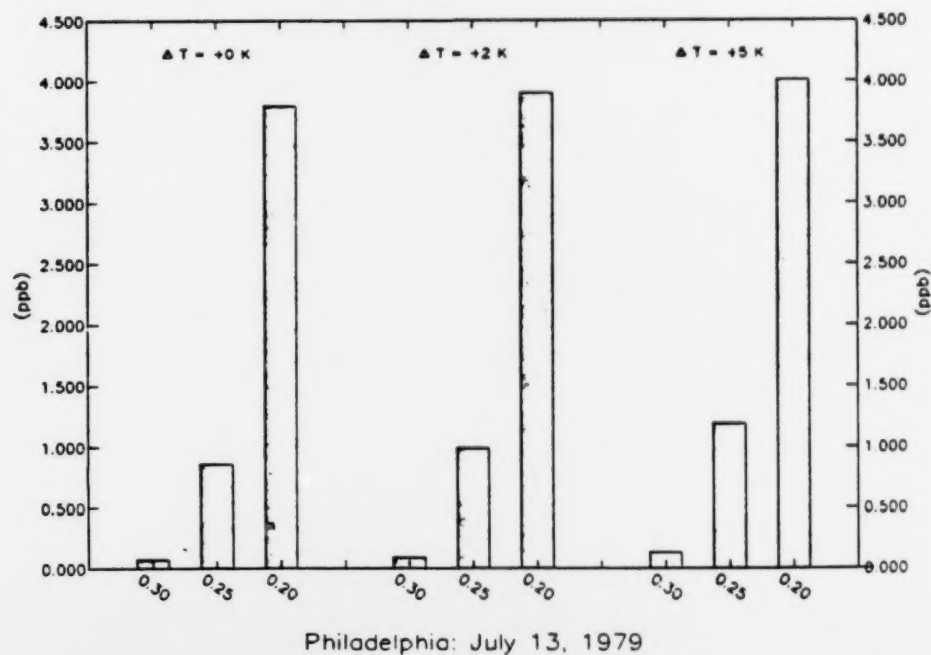
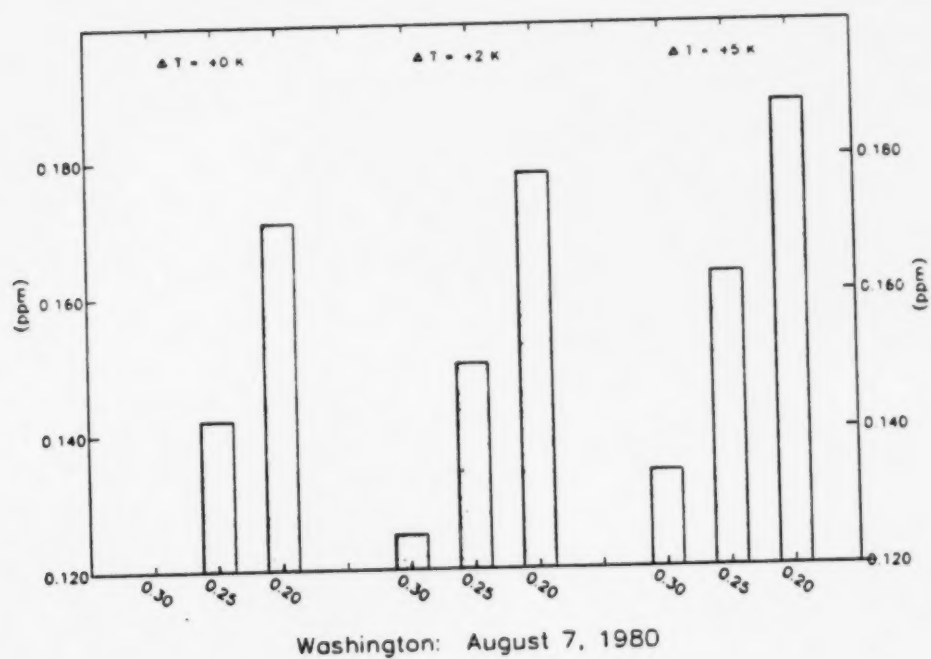


FIGURE 3-6. Results of OZIPM future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania.

OZONE



H2O2

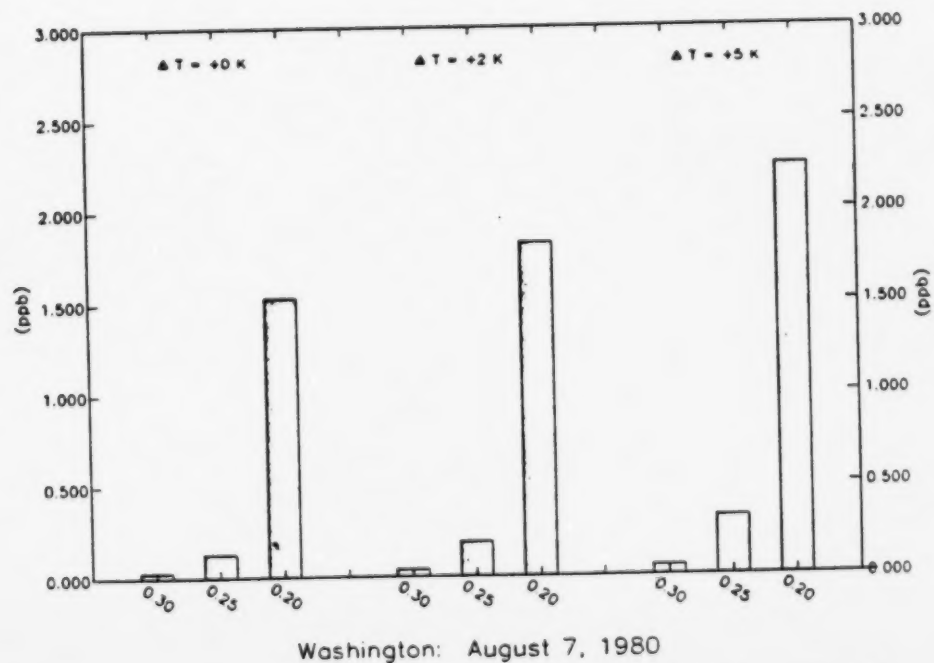
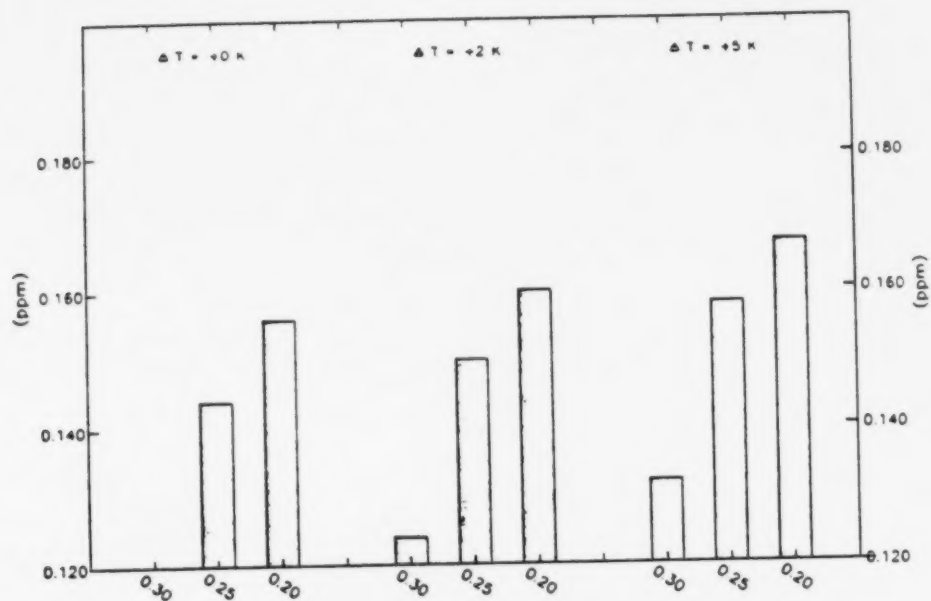


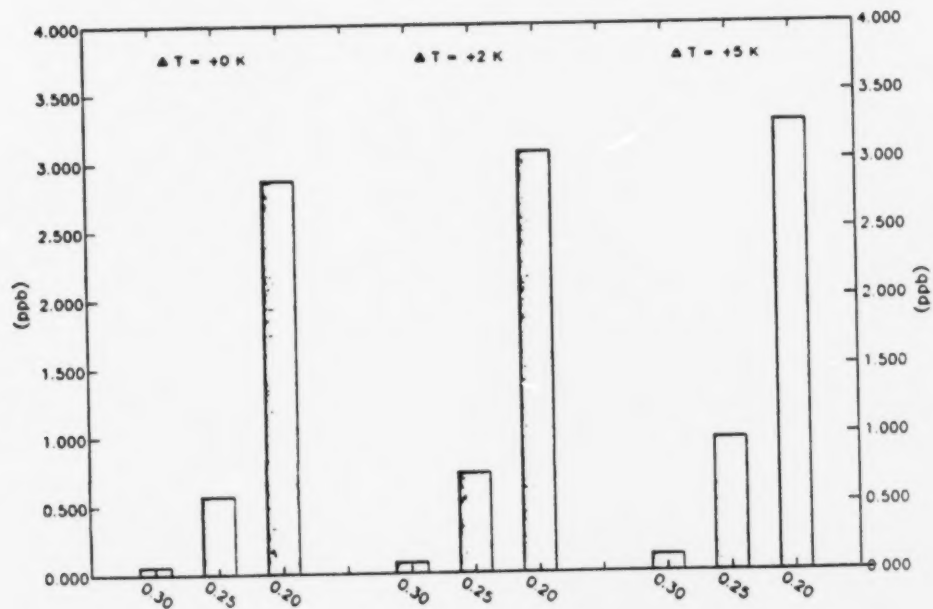
FIGURE 3-7. Results of OZIPM future sensitivity tests for the simulation of 7 August 1980, Washington, DC.

OZONE



Philadelphia: June 24, 1980

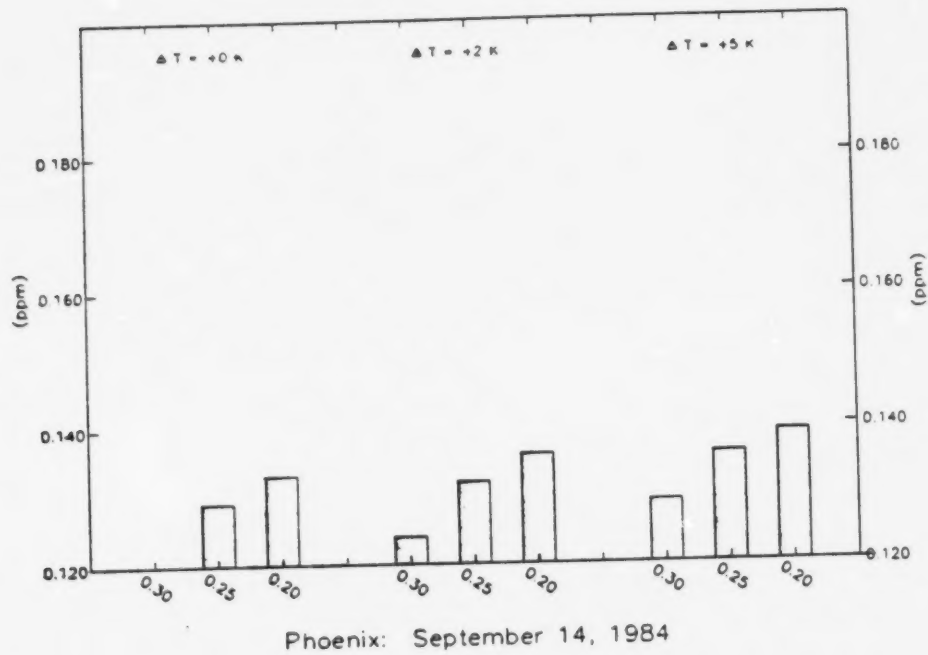
H2O2



Philadelphia: June 24, 1980

FIGURE 3-8. Results of OZIPM future sensitivity tests for the simulation of 24 June 1980, Philadelphia, Pennsylvania.

OZONE



H2O2

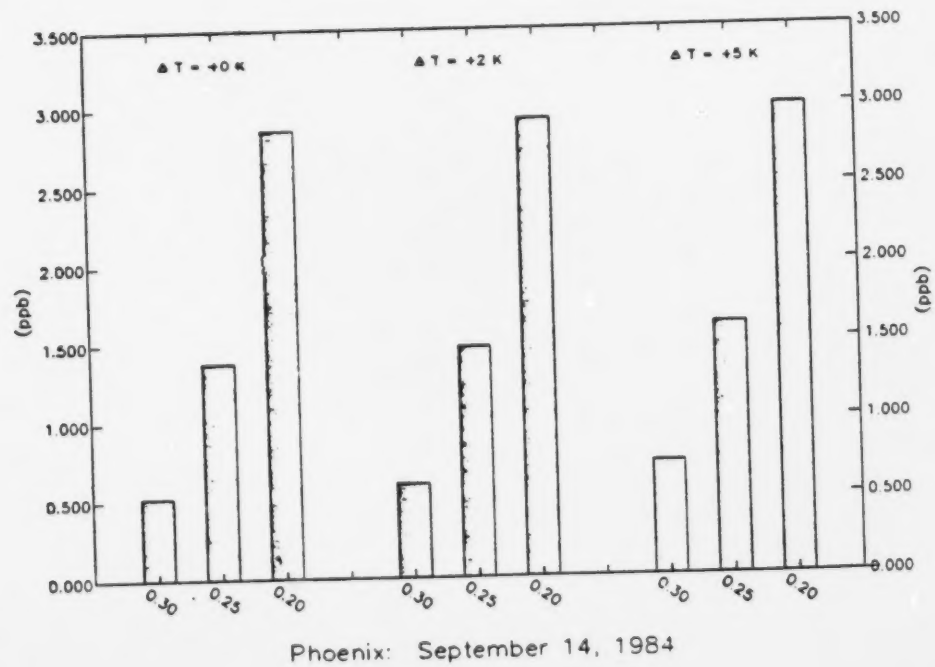
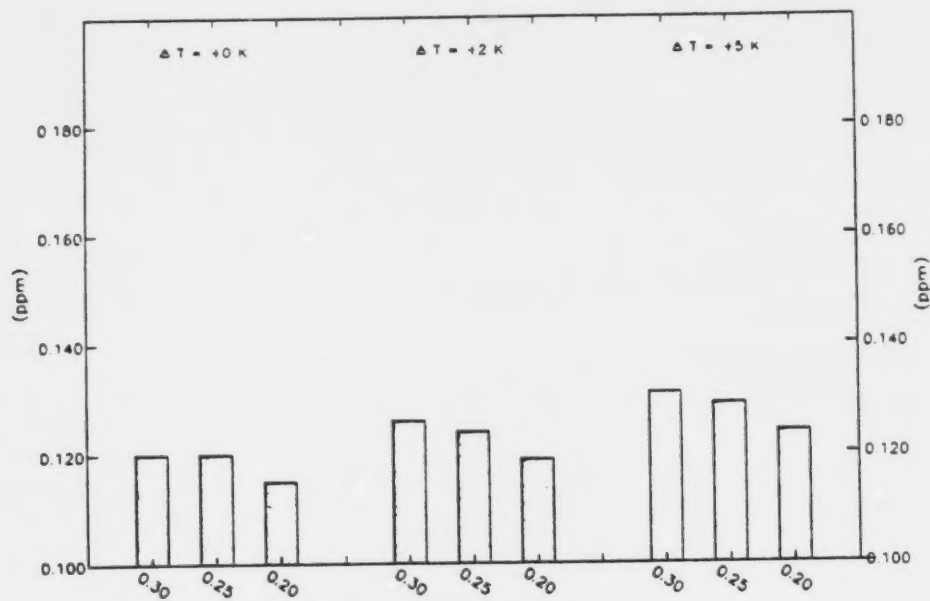


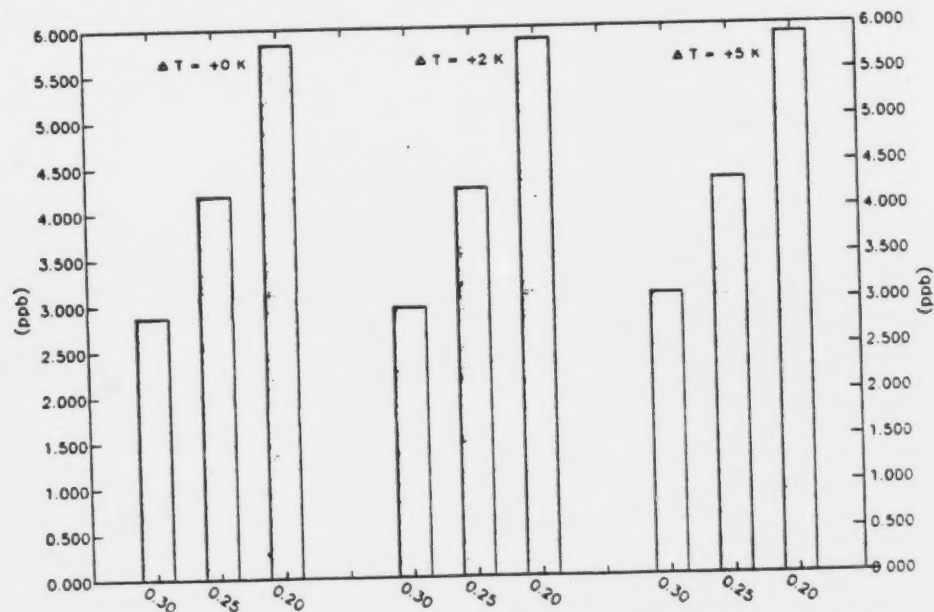
FIGURE 3-9. Results of OZIPM future sensitivity tests for the simulation of 14 September 1984, Phoenix, Arizona.

OZONE



Tulsa: July 1, 1981

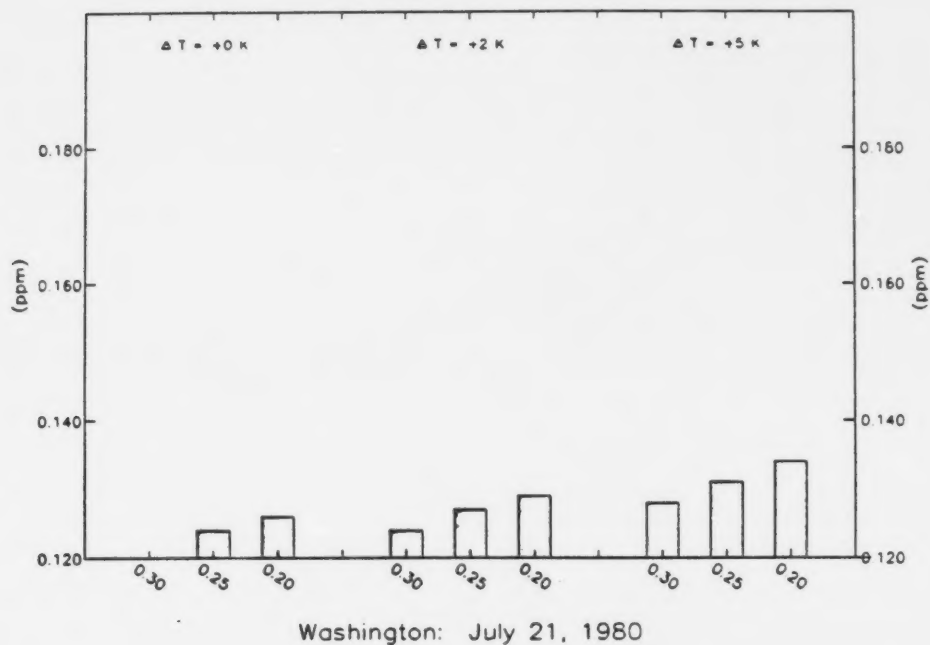
H2O2



Tulsa: July 1, 1981

FIGURE 3-10. Results of OZIPM future sensitivity tests for the simulation of 1 July 1981, Tulsa, Oklahoma.

OZONE



H2O2

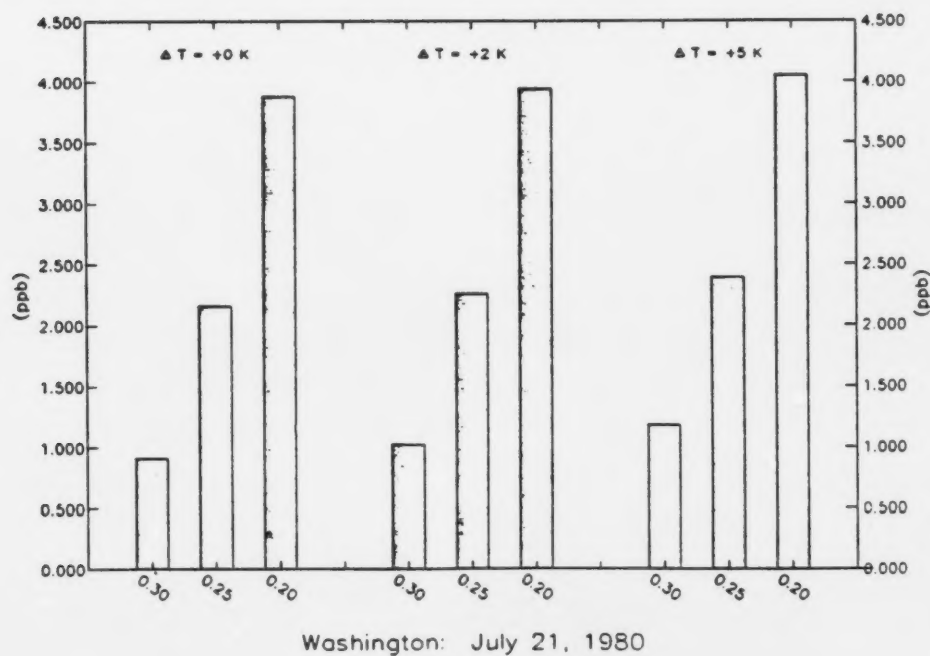
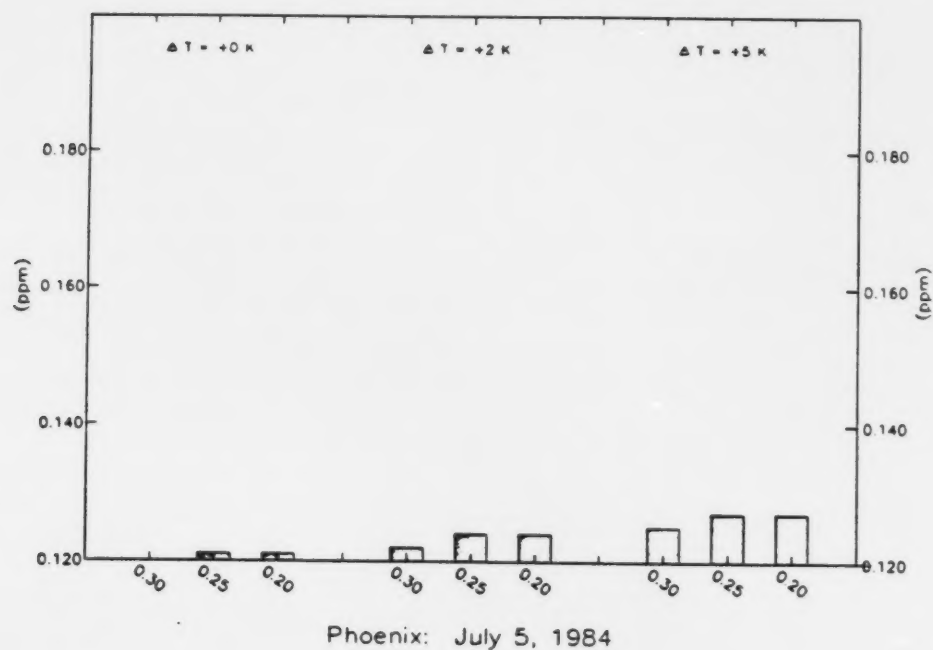


FIGURE 3-11. Results of OZIPM future sensitivity tests for the simulation of 21 July 1980, Washington, DC.

OZONE



H2O2

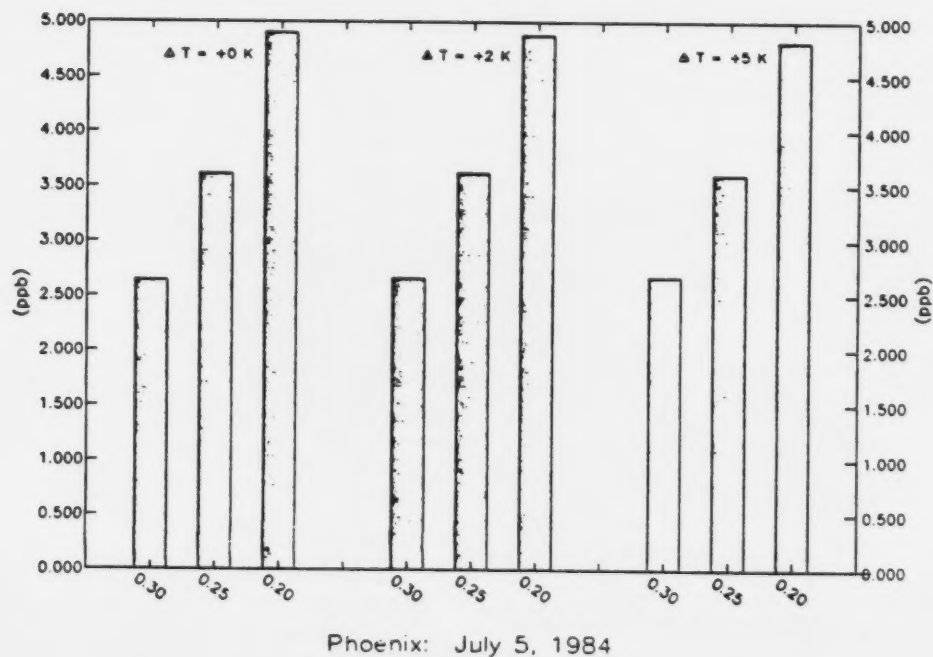
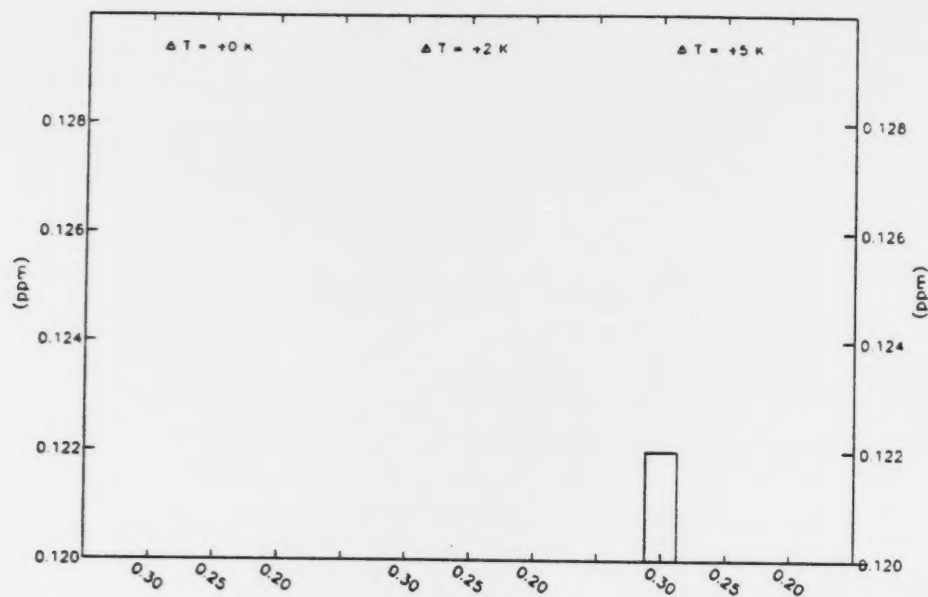


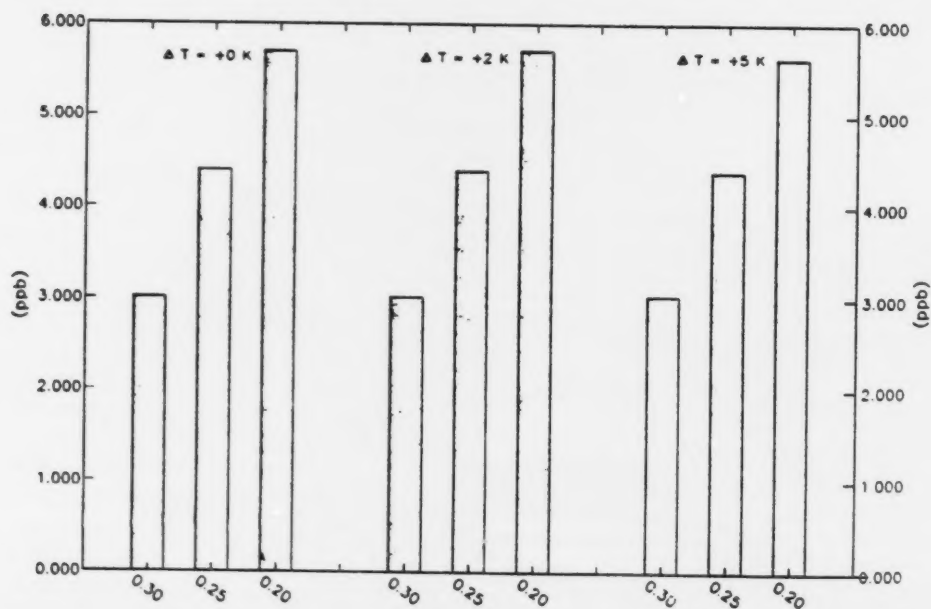
FIGURE 3-12. Results of OZIPM future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona.

OZONE



Nashville: August 10, 1980

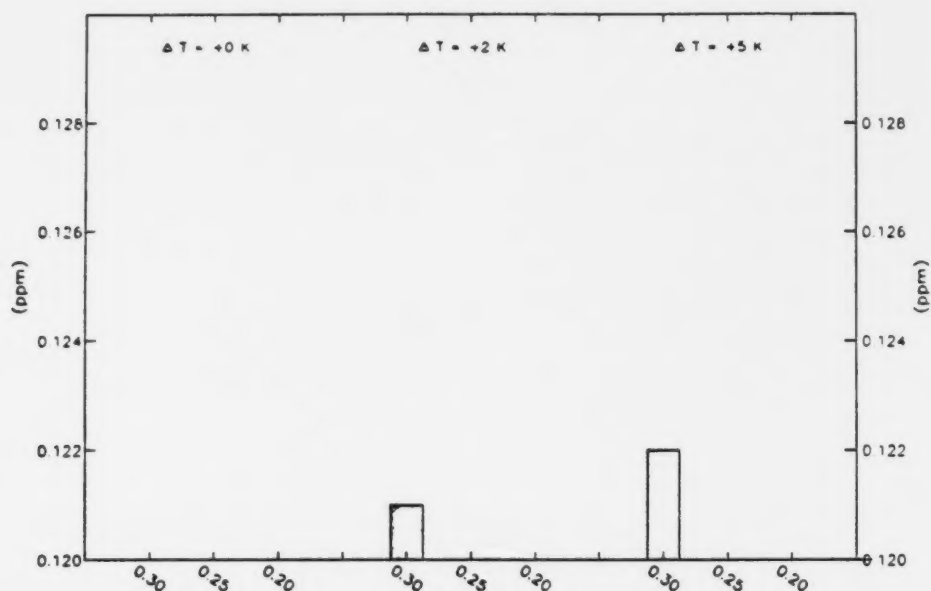
H2O2



Nashville: August 10, 1980

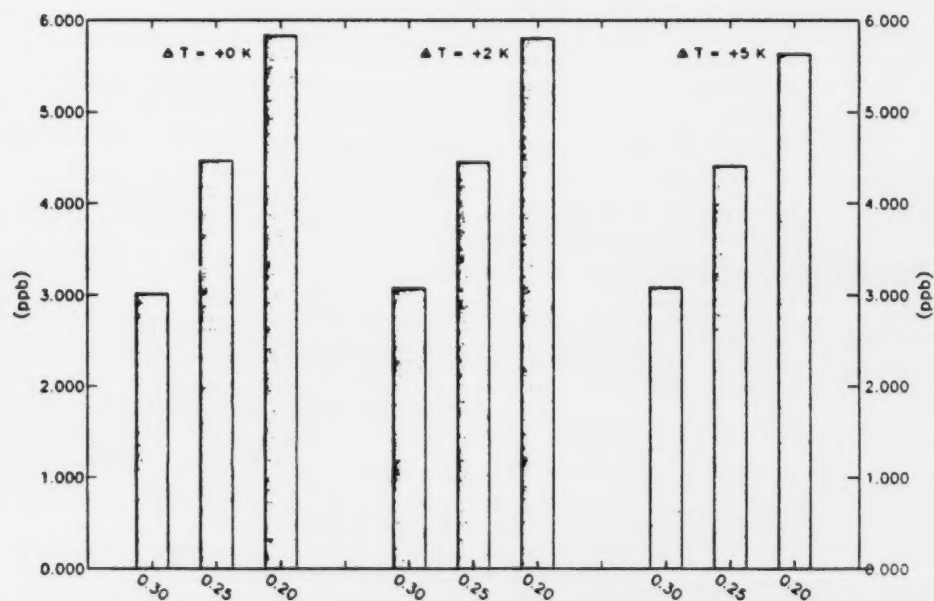
FIGURE 3-13. Results of OZIPM future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 1).

OZONE



Nashville: August 10, 1980•

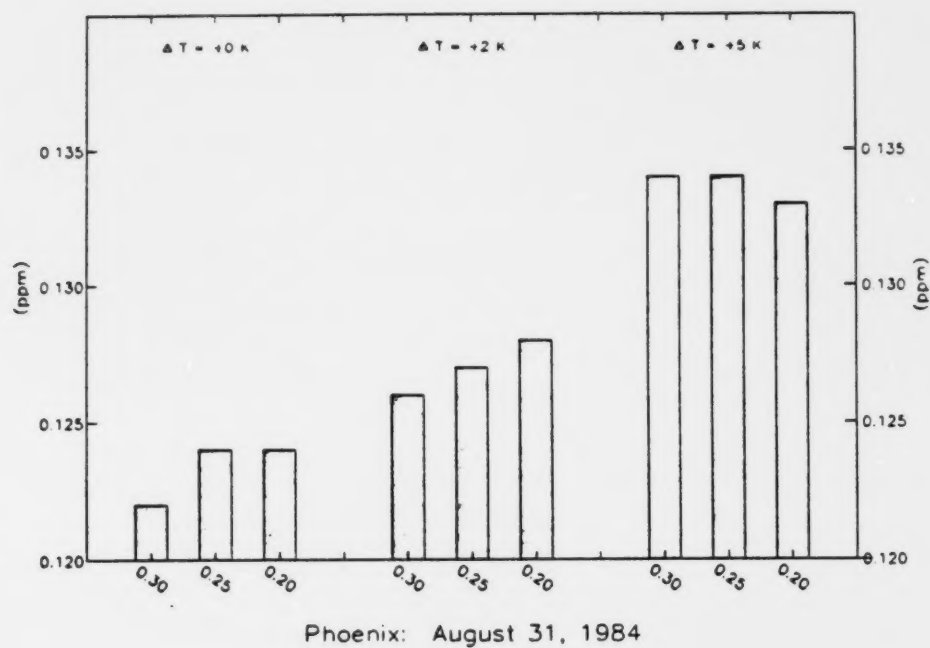
H2O2



Nashville: August 10, 1980•

FIGURE 3-14. Results of OZIPM future sensitivity tests for the simulation of 10 August 1980, Nashville, Tennessee (trajectory number 2).

OZONE



H2O2

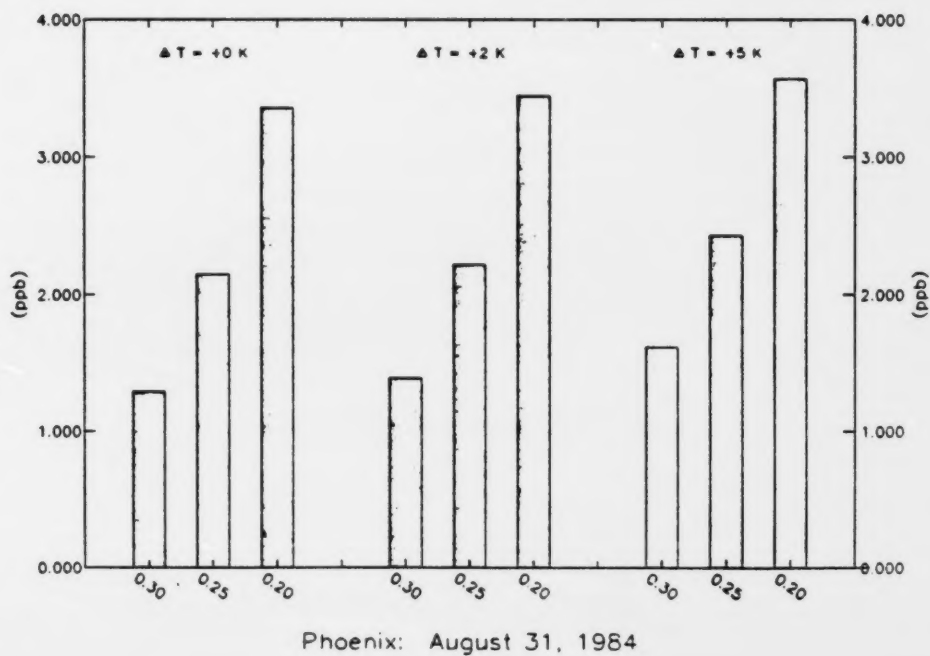
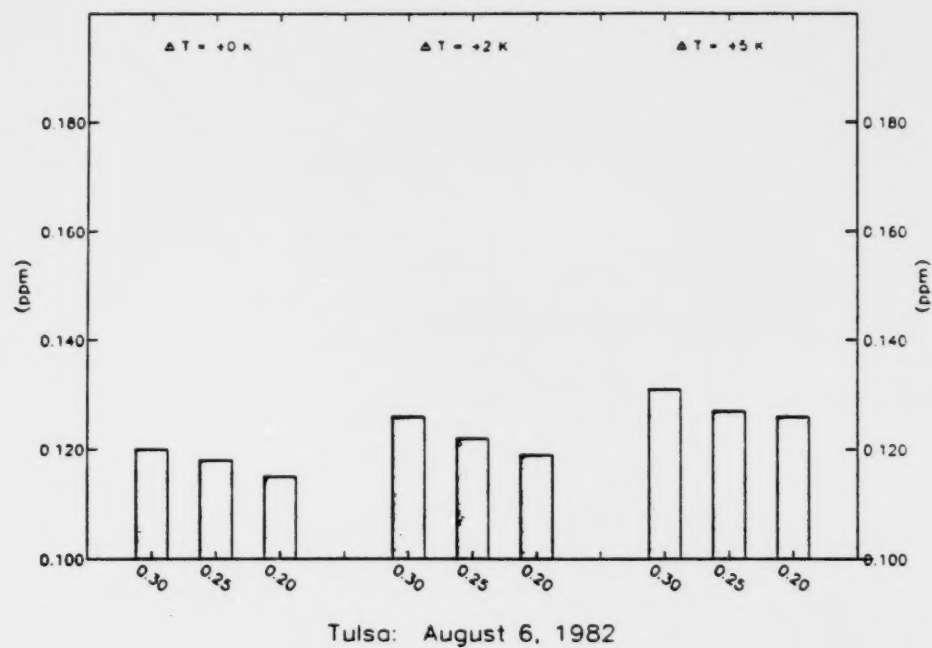


FIGURE 3-15. Results of OZIPM future sensitivity tests for the simulation of 31 August 1984, Phoenix, Arizona.

OZONE



H2O2

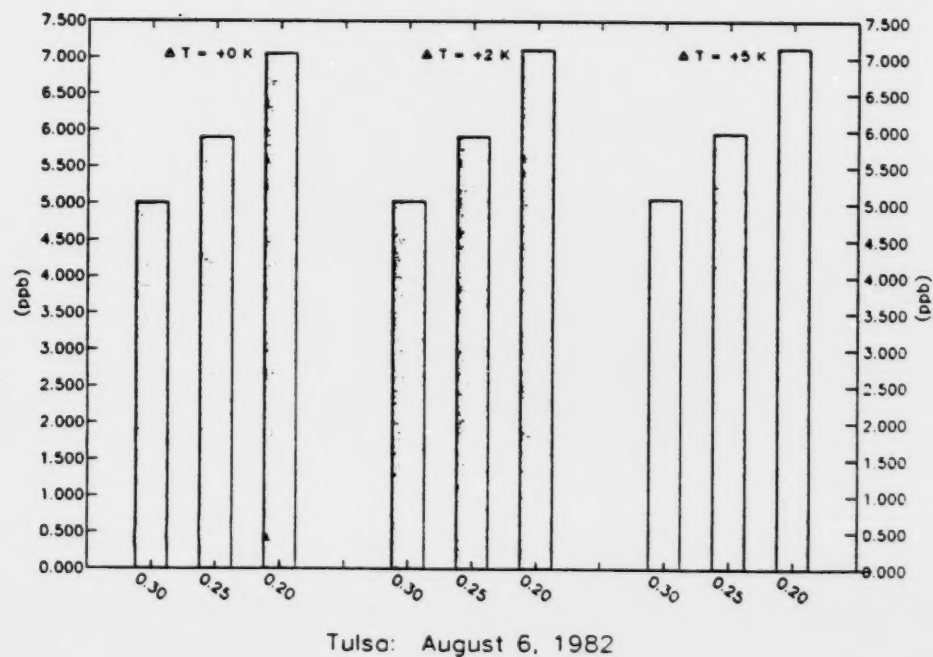
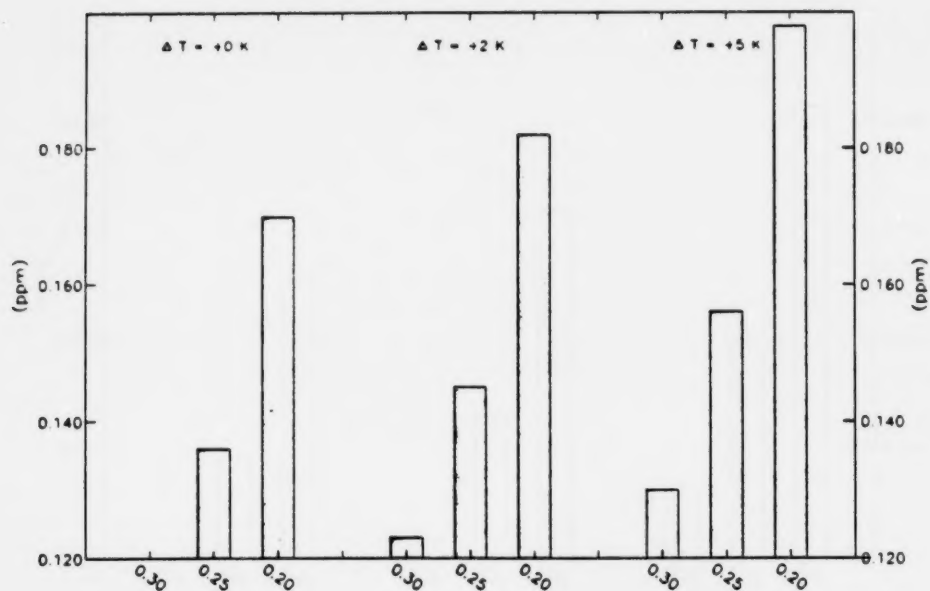


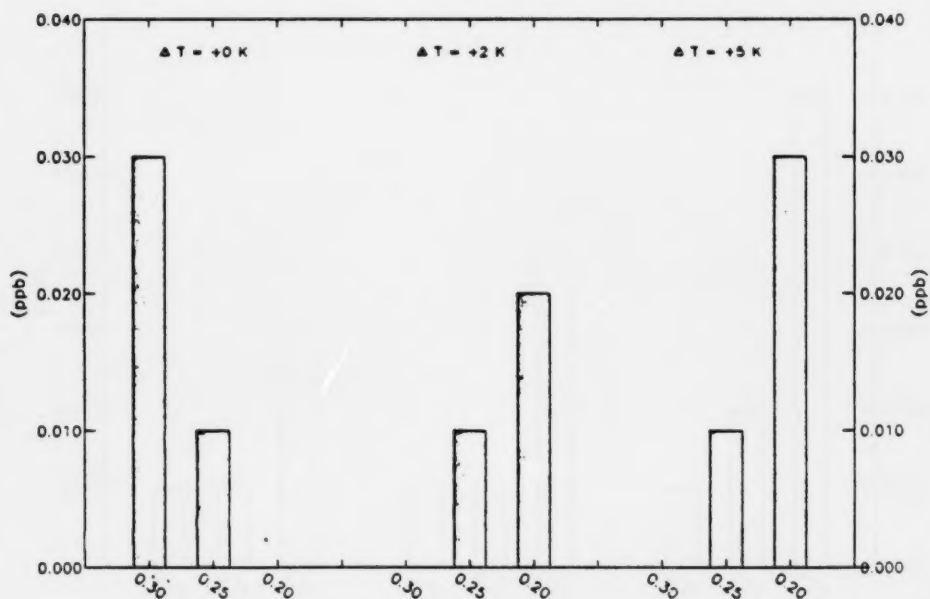
FIGURE 3-16. Results of OZIPM future sensitivity tests for the simulation of 6 August 1982, Tulsa, Oklahoma.

OZONE



Seattle: August 11, 1981

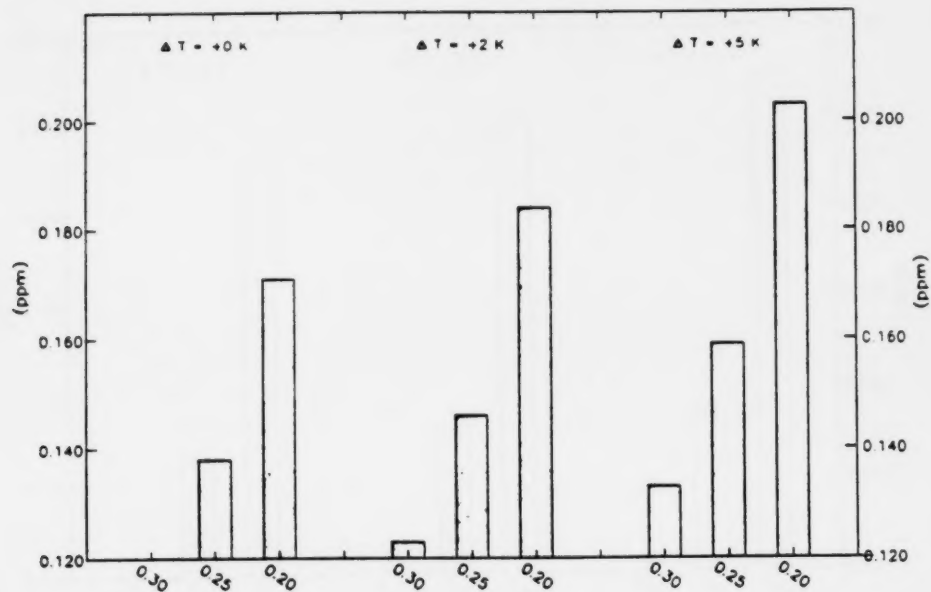
H2O2



Seattle: August 11, 1981

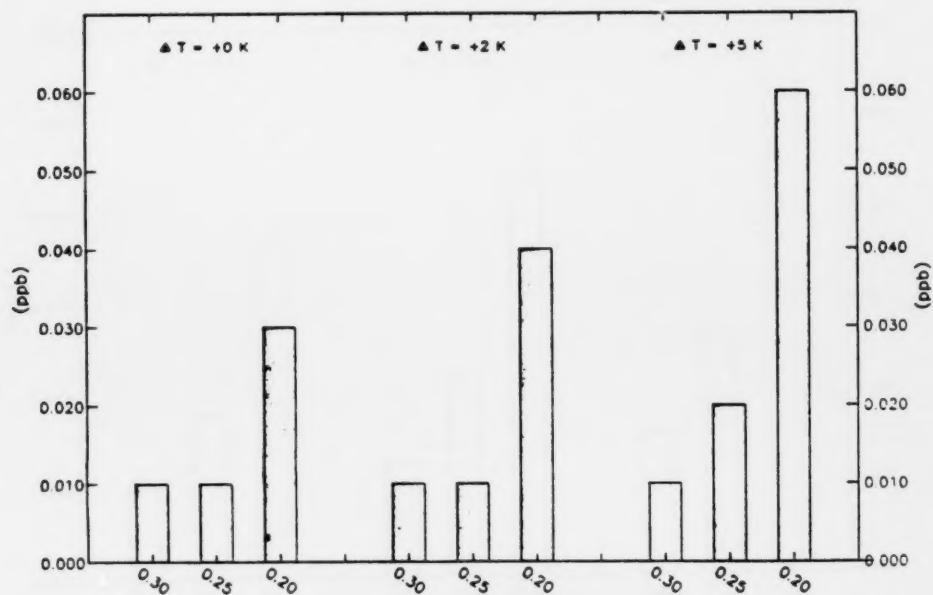
FIGURE 3-17. Results of OZIPM future sensitivity tests for the simulation of 11 August 1981, Seattle, Washington.

OZONE



Seattle: August 7, 1981

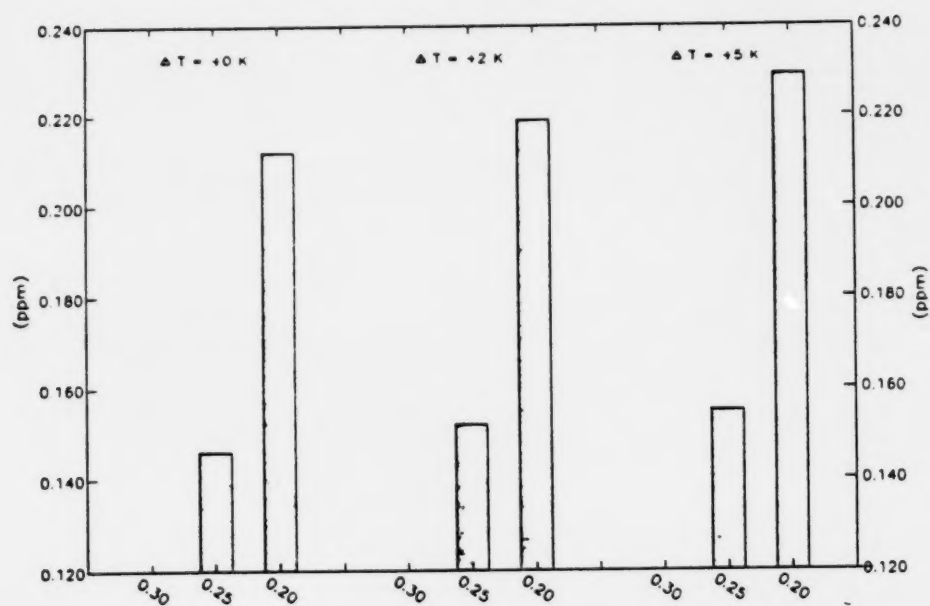
H2O2



Seattle: August 7, 1981

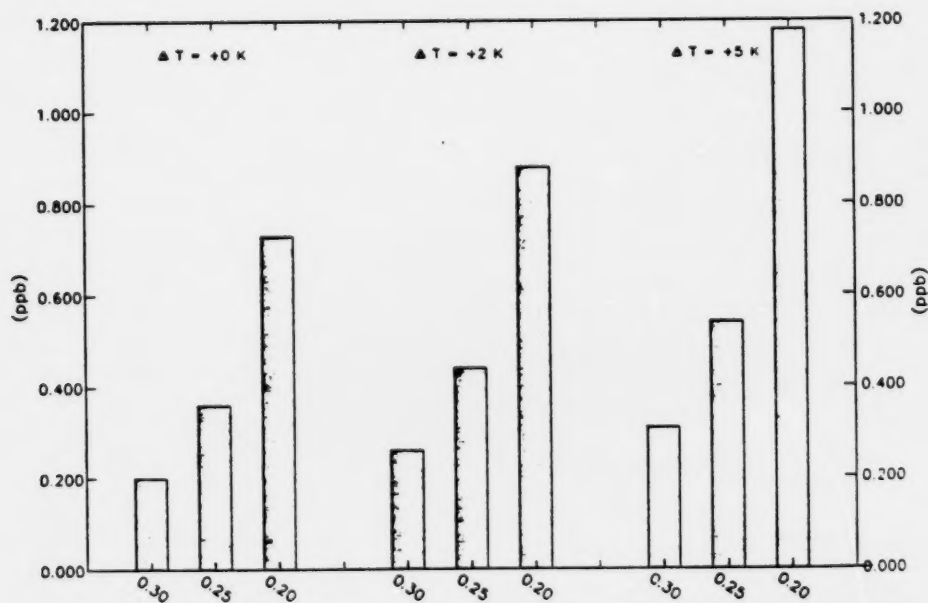
FIGURE 3-18. Results of OZIPM future sensitivity tests for the simulation of 7 August 1981, Seattle, Washington.

OZONE



Los Angeles: June 26-27, 1974

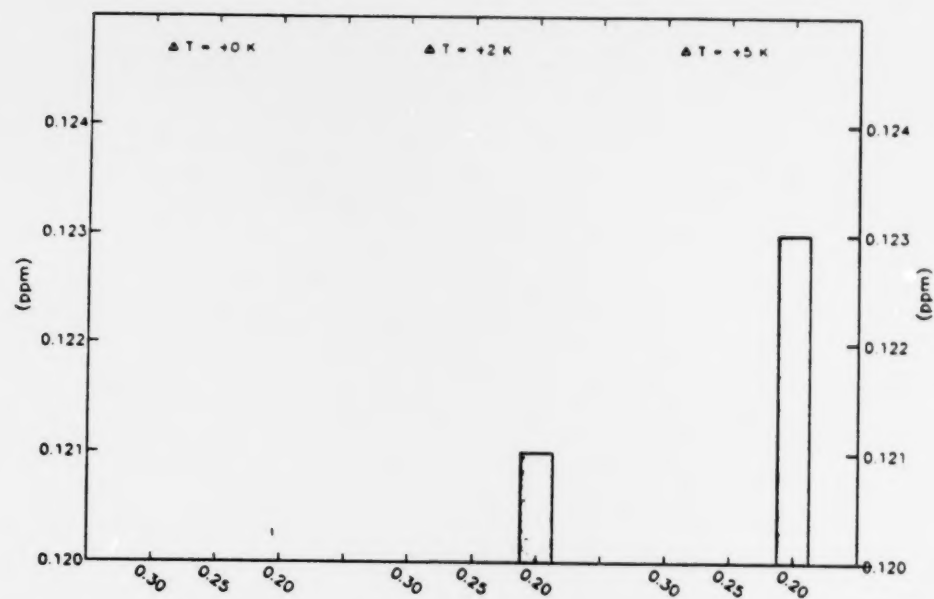
H2O2



Los Angeles: June 26-27, 1974

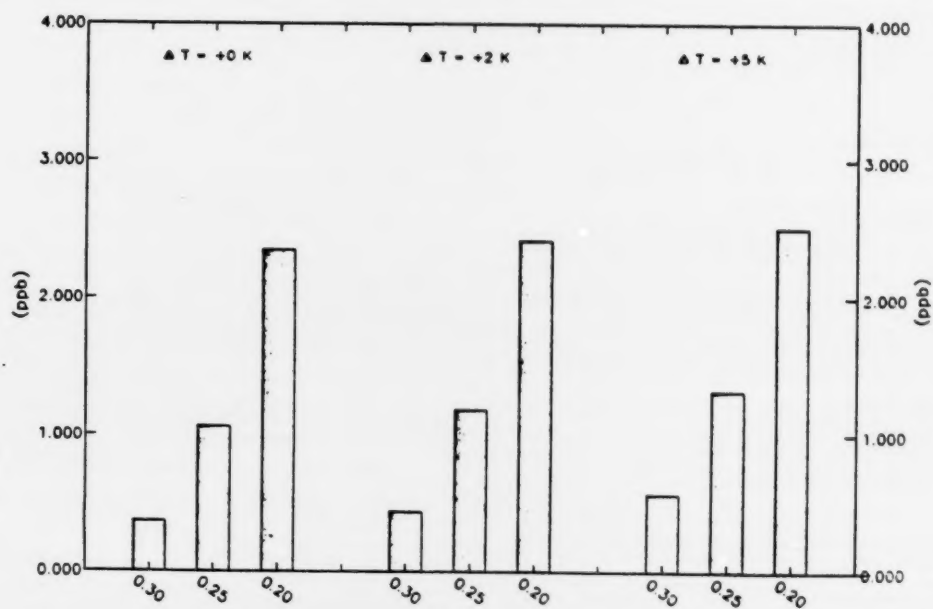
FIGURE 3-19. Results of OZIPM future sensitivity tests for the multi-day simulation of 26-27 June 1974, Los Angeles, California.

OZONE



Compliance Mechanism - Phoenix: July 5, 1984

H2O2



Compliance Mechanism - Phoenix: July 5, 1984

FIGURE 3-20. Results of OZIPM future sensitivity tests for the multi-day simulation of an ozone NAAQS attainment scenario for Pheonix, Arizona.

TABLE 3-21. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the multi-day simulation of 26-27 June 1974, Los Angeles, California.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.115	0.119	0.119	--	3.5	5
250	0.146	0.152	0.155	27.0	32.2	3 .8
200	0.212	0.219	0.229	84.4	90.4	99.1

H_2O_2

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.20	0.26	0.31	--	30.0	55.0
250	0.36	0.44	0.54	80.0	120.0	170.0
200	0.73	0.88	1.18	265.0	340.0	490.0

PAN

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	1.12	1.43	1.76	--	27.7	57.1
250	2.10	2.56	3.18	0.9	128.6	183.9
200	4.10	4.56	5.16	266.1	307.1	360.7

TABLE 3-22. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the multi-day simulation of attainment of the NAAQS in Phoenix, Arizona, using a modified data set from 5 July 1984.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	.100	.104	.108	--	4.0	8.0
250	.114	.116	.119	14.0	16.0	19.0
200	.119	.121	.123	19.0	21.0	23.0

H_2O_2

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.37	0.44	0.57	--	18.9	54.1
250	1.06	1.18	1.32	186.5	218.9	256.8
200	2.35	2.42	2.51	535.1	554.1	578.4

PAN

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	1.83	1.67	1.37	--	- 8.7	-25.1
250	2.12	1.83	1.39	15.8	0.0	-24.0
200	2.25	1.90	1.41	23.0	3.8	-23.0

TABLE 3-23. Maximum hourly concentrations and percentage changes for ozone, H_2O_2 , and PAN for the future sensitivity tests for the simulation of 5 July 1984, Phoenix, Arizona, with the CALL mechanism.

OZONE						
Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	.118	.121	.124	--	2.5	5.1
250	.118	.121	.124	0.0	2.5	5.1
200	.115	.118	.122	-2.5	0.0	3.4

H_2O_2						
Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	2.70	2.72	2.74	--	0.7	1.5
250	3.42	3.45	3.44	26.7	27.8	27.4
200	4.31	4.33	4.34	59.6	60.4	60.7

PAN						
Change in Temp (K)	Concentration (ppm)			Percent Change (from base)		
	0	+2	+5	0	+2	+5
<u>Dobson Number</u>						
300	2.24	1.88	1.42	--	-16.1	-36.6
250	2.45	2.06	1.56	9.4	- 8.0	-30.4
200	2.67	2.30	1.79	19.2	2.7	-20.1

TABLE 3-24. Maximum hourly concentrations and percentage changes for ozone, H₂O₂, and PAN for the future sensitivity tests for the simulation of 13 July 1979, Philadelphia, Pennsylvania, with the CALL mechanism.

OZONE

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	.120	.126	.134	--	5.0	11.7
250	.140	.148	.160	16.7	23.3	33.3
200	.163	.170	.180	35.8	41.7	50.0

H₂O₂

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	0.03	0.03	0.05	--	0.0	66.7
250	0.12	0.19	0.32	300.0	533.3	966.7
200	1.69	2.07	2.57	5533.3	6800.0	8466.7

PAN

Change in Temp (K)	<u>Concentration (ppm)</u>			<u>Percent Change (from base)</u>		
	<u>0</u>	<u>+2</u>	<u>+5</u>	<u>0</u>	<u>+2</u>	<u>+5</u>
<u>Dobson Number</u>						
300	3.27	2.88	2.35	--	- 11.5	- 28.1
250	4.77	4.39	3.79	45.9	34.3	15.9
200	7.27	6.54	5.47	122.3	100.0	67.3

SECTION 4

DISCUSSION OF URBAN SIMULATION RESULTS

Our overall goal in this discussion is the extraction from the urban simulation results of information related to the state of urban photochemical reactivity under potential future conditions of increased surface temperature and ultraviolet radiation. Before presenting this information in its necessarily condensed and tabulated form, we discuss the urban and photochemical processes that act to produce such results by describing typical simulations, focused by the grouping process previously described.

URBAN PHOTOCHEMICAL PROCESSES

Because we want to elucidate photochemical processes that pertain to urban areas under the conditions of this study, we describe simulation results from "typical" test sets representative of each group discussed in Section 3 (a complete discussion of all results from individual test sets would be far too cumbersome for this report). Our discussions and the figures used to show concentration changes will focus on extreme future conditions (+0 and +5 K, and 0.300 and 0.200 cm-atm overhead ozone column) to clearly isolate the specific chemical processes and types of effects that occur. Overall trends across the range of changes in the study are addressed in our analysis of all results following this discussion of dynamic processes.

Ozone

We begin our discussion of possible changes in urban photochemical processes with the Group 1 test sets. These data sets represent non-attainment days requiring substantial control of NMOC to comply with the ozone NAAQS. All base-case simulations for Group 1 produced a maximum hourly average ozone concentration of over 0.17 ppm. As a representative future simulation set, we have chosen the 13 July 1979 tests for Philadelphia (the Los Angeles simulations are discussed with the multi-day tests).

Figure 4-1 provides future simulation results for 0.300 and 0.200 cm-atm overhead ozone columns at measured and +5 K temperature profiles. The +0 K/0.300 cm-atm scenario is the future base case of ozone NAAQS attainment. As with all simulation results shown, the ozone, NO_2 and H_2O_2 traces are more distinctly separated for the ozone column changes than for the assumed temperature changes. Therefore, the groupings found in most figures for ozone and H_2O_2 show the 0.200 cm-atm results far above the 0.300 cm-atm results, and the +5 K simulations as slightly more reactive than the +0 K runs. For NO_2 , an oxidant precursor that is eliminated more rapidly in more reactive systems, these trends are reversed. In the case of PAN, recall that peroxyacyl compounds exhibit some of the most extreme temperature-dependent behavior of all atmospheric compounds. Hence, PAN concentrations are lower for higher temperature simulations due to their much higher decomposition rates (see Figure 4-1).

A key result that can be extracted from this plot and those to follow is that an increase in ultraviolet irradiance tends to enhance short-term reactivity in a photochemical system. This results in a more rapid ozone formation rate early in the day because oxidant precursor species are plentiful. However, since the afternoon maximum ozone concentrations depend on afternoon precursors, which can be significantly depleted by enhanced reactivity in the morning, the short-term trends cannot always be equated with long-term reactivity measures such as maximum afternoon ozone concentrations.

In the case of the Group 1 test data, NO_x and NMOC emissions are high enough throughout the day that the emissions reduction required to attain the ozone NAAQS still allows sufficient precursors to exist (or accumulate) late in the afternoon during attainment conditions. Note also that the ozone concentration is still increasing at the 1800 hour of the attainment simulation, indicating additional oxidant-forming potential at the end of the EKMA calculation period for those conditions. Increased energy input to such a system (due to future changes in surface temperature or stratospheric ozone) provides increased reactivity, and therefore, more efficient utilization of these precursors to form additional ozone and oxidant products. This is evident in Figure 4-1, where more extreme reactivity (from the 0.200 cm-atm overhead ozone column) consumed most of the NO_2 faster, producing ozone and PAN more rapidly, and resulting in enhanced H_2O_2 production. Higher PAN production can also affect continuing reactivity since its decomposition near the end of the day contributes acetyl peroxy radicals and NO_2 back into the reactive mixture.

To represent simulations in the Group 2 cities, we selected the results of the 21 July 1980 Washington DC and 1 July 1981 Tulsa simulations (Figures 4-2 and 4-3). Recall that these cities required moderate NMOC control

Philadelphia, PA - 13 July 1979

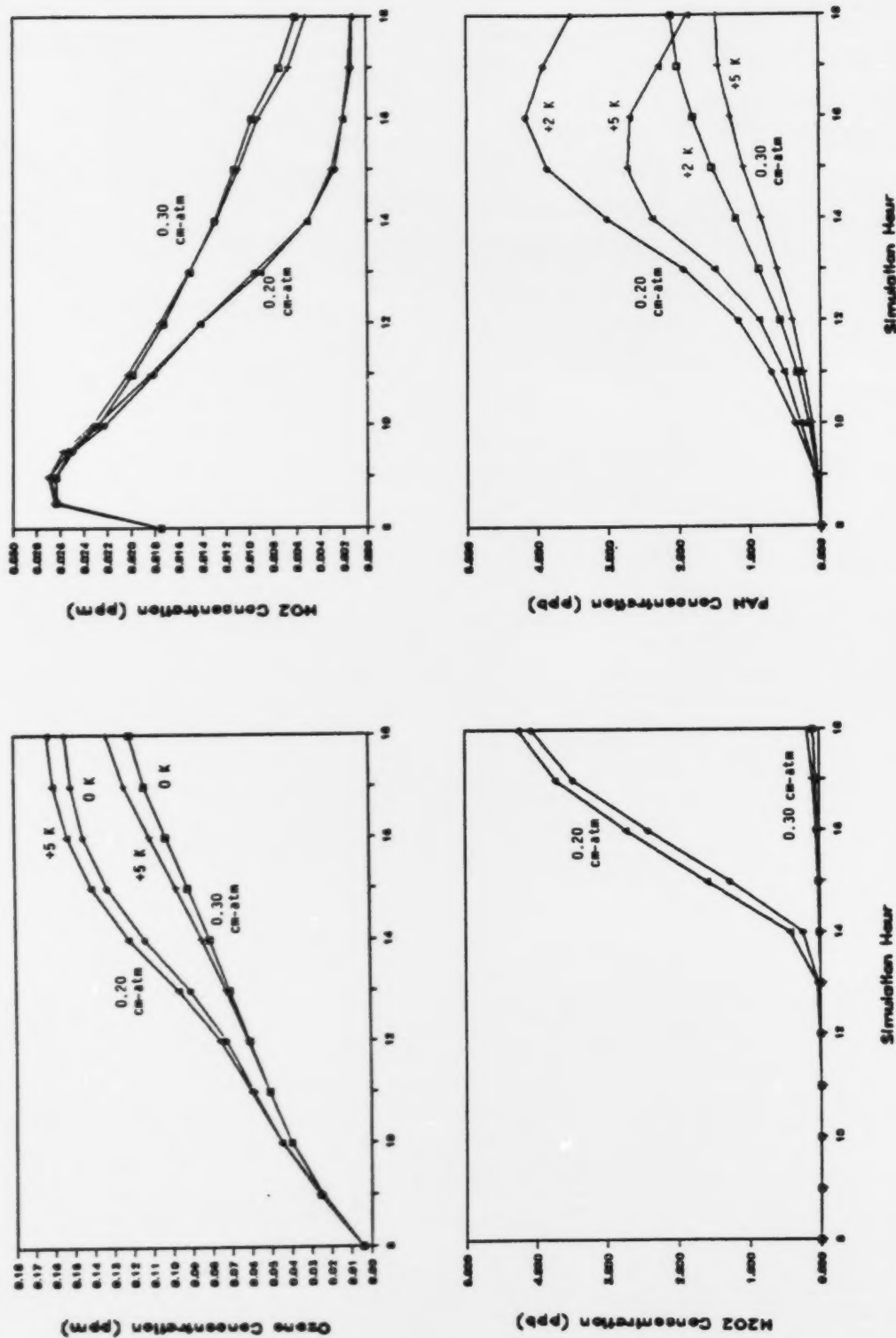


FIGURE 4-1. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests-- simulation of 13 July 1979, Philadelphia, Pennsylvania.

Washington, DC - 21 July 1980

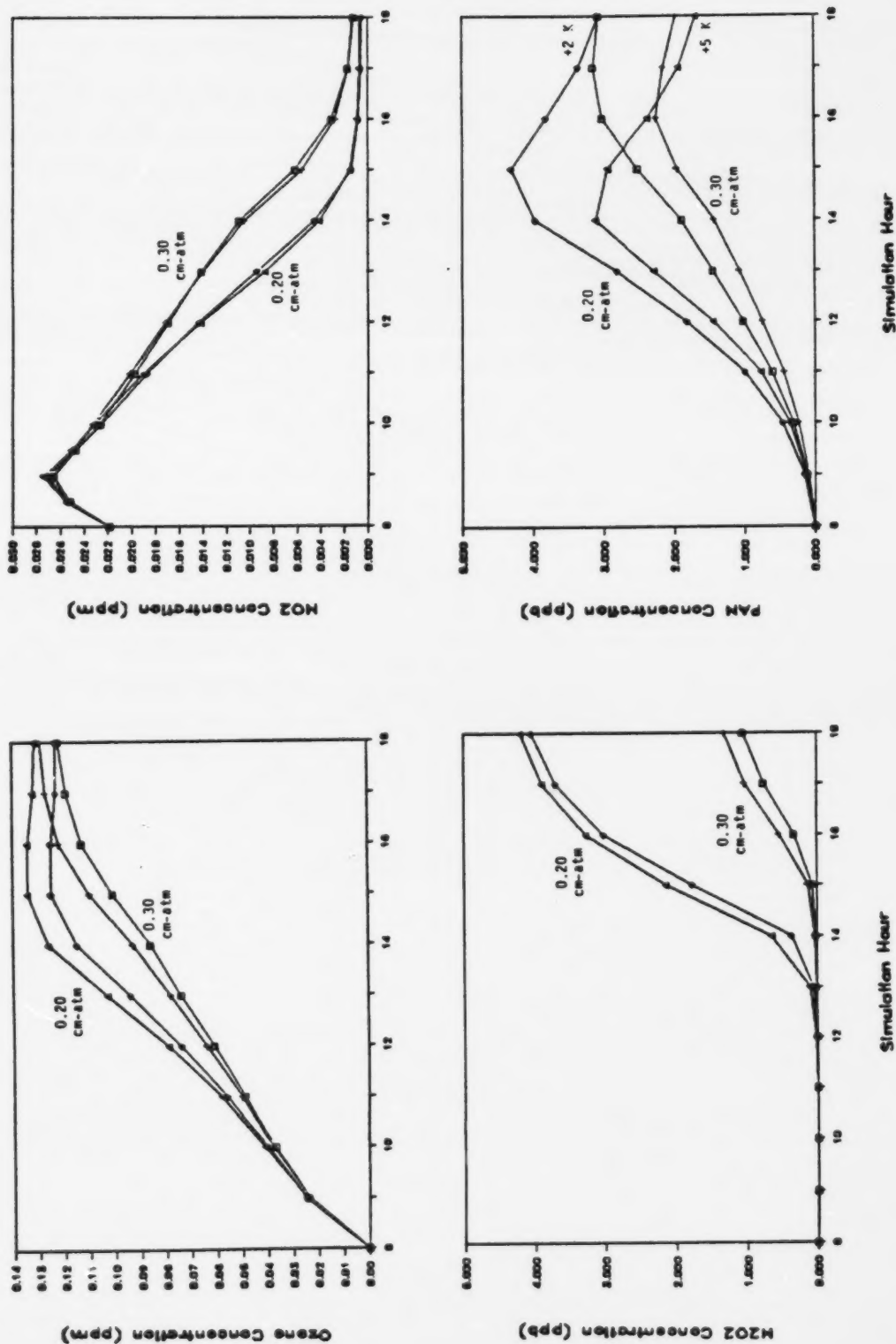


FIGURE 4-2. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 21 July 1980, Washington, DC.

Tulsa, OK - 1 July 1981

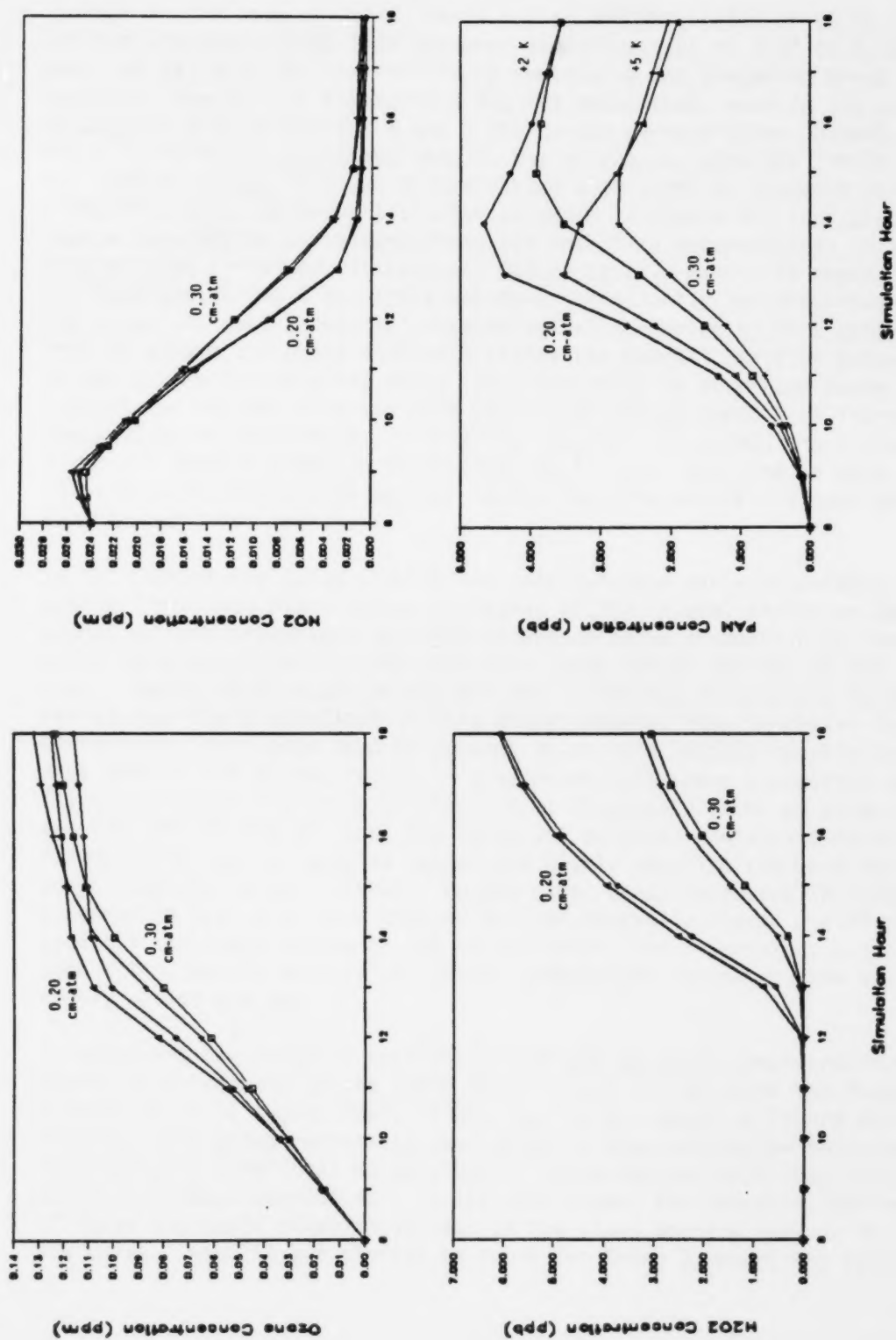


FIGURE 4-3. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests-- simulation of 1 July 1981, Tulsa, Oklahoma.

(except in the case of Tulsa, which had an NMOC/NO_x ratio of 25.5) to achieve the ozone NAAQS from measured concentrations of 0.17 to 0.14 ppm. We can describe the results by continuing the preceding Group 1 discussion. Analysis of Figures 4-2 and 4-3 shows that, even in the ozone attainment simulations (+0 K and 0.200 cm-atm overhead ozone column), the NO₂ concentration approaches zero in the afternoon, with the result that the rate of change in ozone concentration also tends to approach zero. Comparison with the Group 1 simulation shown in Figure 4-1 indicates that such a termination of oxidant-formation potential occurred only in the more extreme (enhanced ultraviolet) future cases. Hence, it appears that the moderate, Group 2 scenarios may have sufficiently low precursor loading rates and more beneficial meteorological scenarios so that control of NMOC to attain the ozone NAAQS diminishes the overall reactive potential of the system to the point where large increases in afternoon ozone concentrations are not observed with additional energy input from increased temperature or ultraviolet irradiance. However, as noted, these simulations all predict enhanced short-term reactivity, resulting in more rapid rates of ozone production earlier in the day (and possibly closer to more densely populated areas).

In the case of the Tulsa simulation, this enhanced early reactivity due to future diminished ozone column densities (0.200 cm-atm) serves to deplete enough oxidant precursors to limit afternoon ozone production to levels below those predicted for the base-case ozone column density (0.300 cm-atm). Again, this result points out one of the key differences to be discerned from the predictions in this study; namely, that increases in ultraviolet irradiance tend to enhance short-term, midday reactivity in ways that do not always result in greater overall ozone production because (1) the greatest increases in ultraviolet irradiance occur at solar noon, and (2) the results of these increases are enhanced photolysis rates and formation of radical species (which are highly reactive and have very short atmospheric half lives). On the other hand, increases in surface temperature over the range studied provide generally higher yields of oxidants and lower yields of PAN in all cases, for all periods during the simulation, mainly because the future temperature increases were applied evenly across the day.

To represent the group of test cases with design ozone concentrations nearly in attainment of the ozone NAAQS (Group 3), we chose the Phoenix, simulation of 31 August 1984. These results are shown in Figure 4-4. Ideally, this group represents days on which moderate-to-low emissions are combined with beneficial meteorological scenarios to yield less reactive ozone production conditions. In the data shown, for instance, the effect of large and rapid dilution is seen in the steep morning decline of the NO₂ curve. Results are similar to those for Group 2, where the rate of

Phoenix, AZ - 31 August 1984

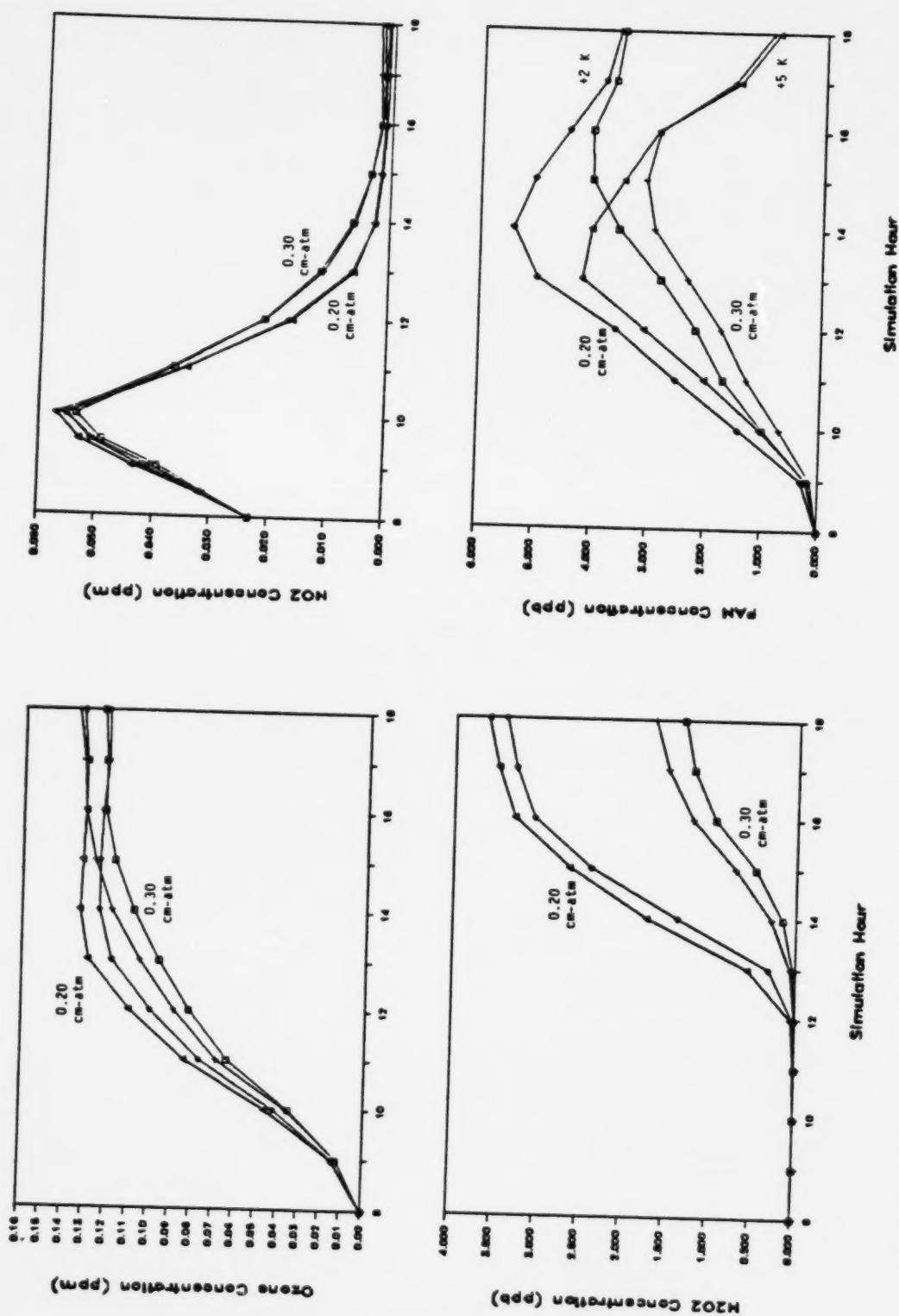


FIGURE 4-4. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 31 August 1984, Phoenix, Arizona.

morning oxidant production is larger with more energetic future conditions, but depletion of precursors by midday limits the overall amount of ozone that can be produced. In fact, in cases where large dilution occurs with morning mixing height rise, the effects of additional ultraviolet radiation may be further countered since the increased rate of oxidant formation will cause ozone production to occur earlier, during the period of high morning dilution. This brings to light the fact that changes in global climate due to Greenhouse warming will affect parameters other than temperature at the surface. Some of these additional factors, which can only be addressed here in a cursory manner, could be the rate of change in mixing depth, amount of cloud cover, wind speeds, and water vapor concentrations.

In this discussion we have begun to touch on some interesting characteristics of photochemical dynamics in possible future airsheds. As with the present-day issue of urban ozone control, the magnitude of the potentially harmful affects of photochemical smog formation can be related to what is loosely described as the oxidant-forming potential of the urban system. This, in turn, is generally thought of as a function of meteorological conditions (mixing depth, temperature, etc.) and the efficiency with which an individual urban atmospheric system can chemically convert precursors to oxidant. This efficiency, sometimes also described as reactivity, can differ due to the location of an urban area (i.e., the variations in solar elevation at different latitudes) and will certainly vary due to the changes in ultraviolet irradiance or surface temperatures as studied in this investigation. We view this concept of reactivity as a short-term measure of chemical rates (such as the rate of ozone formation, rates of precursor decay or the mass flux through various radical reaction paths), whereas oxidant-forming potential relates more closely to the maximum concentration of oxidant that could be formed under various conditions for a given level of precursors (depleting all or most precursors in the process). The future scenarios always show increased reactivity with more energy input (due to either enhanced ultraviolet irradiance or temperature) but do not always indicate additional oxidant-forming potential when compared to the future base case.

In the Group 1 test sets we noted both increased reactivity (in the form of more rapid precursor depletion and ozone formation) and increased oxidant-forming potential as higher amounts of ozone are formed at the end of the day. The Group 2 and 3 scenarios also indicated greater reactivity, but showed far less oxidant-forming potential, and sometimes produced less ozone for the future cases. This appears to be mainly because oxidant precursors were already sufficiently depleted in the Group 2 and 3 future base cases (+0 K and 0.300 cm-atm) to have achieved nearly the maximum ozone-forming potential for those days. Additional energy input in the non-base-case scenarios used the precursors more efficiently to produce

ozone faster, but did not result in significantly higher ozone concentrations. In the Group 1 tests, however, the future base-case scenarios were created on the basis of control of ozone to 0.12 ppm at 1800 hours (the EKMA completion point). At that point, sufficient precursor species and emissions remained to result in a still-increasing ozone slope; indicating that the full oxidant-forming potential of the system was not yet realized. Therefore, the future Group 1 scenarios not only produced oxidant more rapidly, but they utilized the precursors more efficiently to generate higher concentrations of ozone in the time allotted. The difference here appears to be one of the range over which the original EKMA calculations were made. Extension of the EKMA termination time past 1800 hours would probably yield higher NMOC control requirements, providing less future sensitivity, because more of the oxidant-forming potential of those days was actually accounted for. To provide an even more extreme example, we now discuss the Group 4 data.

As stated in our earlier discussion of Group 4 data, we feel that the NMOC and NO_x measurements that contributed to the OZIPM input data are rather uncertain for these simulations. The sampling period appears to have been only one week for a very limited monitoring network. In addition, it is not clear whether the morning inversion height was actually 250 m, or whether that value was assumed. A lower morning layer would provide additional dilution around midday. On the other hand, since these precursor and mixing height values were used in the Washington SIP and do present a unique future scenario, we briefly discuss them here.

We use the results of the 11 August 1981 simulation for Seattle, (Figure 4-5) as our example of a Group 4 future sensitivity test. The interesting aspect of these data is the persistence of high levels of NO_x throughout the simulation. As we saw with the Group 1 data, the availability of oxidant precursors near the end of the day in the future base-case scenario can represent unused oxidant-formation potential. When additional radiant or thermal energy is input to the system through future scenarios of stratospheric ozone depletion or surface temperature increases, much higher levels of oxidant and oxidized products are predicted to be formed. We also see a similarity with the Group 1 tests in the fact that the future base cases generated from EKMA control calculations do not account for the overall oxidant-forming potential of the simulated chemistry, but only that up to 1800 hours. The control calculations for Groups 2 and 3 apparently accounted for a larger portion of their potential, since most design ozone was formed before 1800 hours. Hence, the more extreme Group 2 and 3 future scenarios produced ozone faster, but did not yield significantly different amounts from the future base-case values (0.12 ppm).

Seattle, WA - 11 August 1981

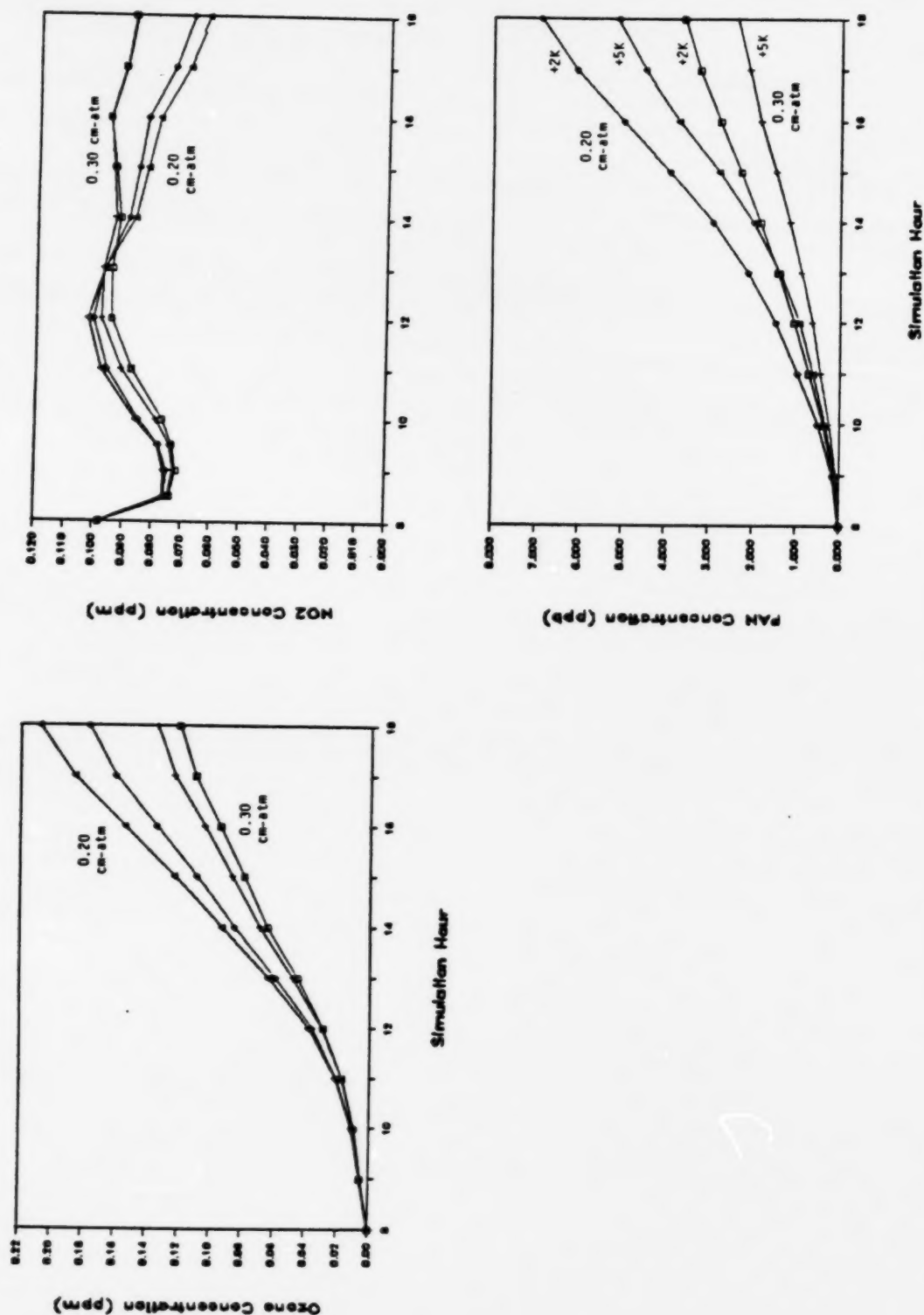


FIGURE 4-5. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests--simulation of 11 August 1981, Seattle, Washington.

The difference between the Group 1 and Group 4 test sets is that though Seattle does not have a high precursor loading rate throughout the day (such as in the Los Angeles Basin or the Northeast Corridor regions), a combination of meteorological and emissions effects results in a high sensitivity to future changes. As noted, these include the more northerly location (lower light intensity), higher initial NO_x concentrations, and limited mixing height rise (providing a parcel with only about 40 percent of the volume of a typical Group 1 simulation). The combined effect of these factors was to initially yield only a small NMOC emission control requirement from the EKMA calculation, because the lower light intensity and high NO_x concentrations limited ozone formation to a period later in the day when solar energy input was diminishing. Therefore, under present conditions, the Group 4 air parcels require little NMOC control to achieve the ozone NAAQS (see Table 3-5). However, because these test cases are precursor-rich and energy-limited, the future base case (NAAQS attainment for ozone) scenarios appear to be near an energy "threshold" where additional energy (such as the enhanced ultraviolet irradiation caused by stratospheric ozone depletion) could provide significant impetus for increased afternoon reactivity by more efficiently utilizing the ozone precursors. Therefore, though both the data and simulations must be verified, these results show sensitive future scenarios not completely like the emissions-oriented Group 1 simulations. The Group 4 tests combine a number of variable factors into a situation where, with the increased energy of potential future global changes, a "threshold" may be crossed and a rather dormant urban photochemical system can now achieve a large fraction of its oxidant-forming potential.

Hydrogen Peroxide and Other Products

Up to now, we have only briefly described H_2O_2 concentrations and production rates. We expand that description by discussing the overall chemical dynamics of a typical system. A detailed explanation of the specific photolytic and chemical processes that vary significantly with enhanced ultraviolet irradiance has been provided in Section 2. Generally, the enhanced ultraviolet irradiance expected to result from stratospheric ozone depletion should increase surface photolysis rates in the troposphere, providing higher production rates (and therefore, higher concentrations) of radical species. The two key reactions to be enhanced appear to involve the photolysis of ozone to $\text{O}(^1\text{D})$ and formaldehyde to radical products (two H radicals per formaldehyde molecule). As we have already noted, $\text{O}(^1\text{D})$ provides two OH radicals upon reaction with water vapor, and H radicals react rapidly with atmospheric O_2 to form HO_2 radicals. These

two species are highly reactive and, therefore, occur at very low concentrations. In simulations of urban photochemistry, traces of their concentrations can be used as indicators of the extent of photochemical oxidation processes.

Consider the results of future sensitivity simulations for the Philadelphia data set of 24 June 1980 provided in Table 3-6 and Figure 4-6. These results are similar to the earlier Group 1 future scenario data in that the 0.200 cm-atm case consumed NO_x at a greater rate during the afternoon, resulting in additional reactivity and greater ozone production. Also, from these and the earlier data, it is apparent that H_2O_2 production is extremely sensitive to increases in ultraviolet irradiance. Referring to Figure 4-6, this can be delineated in a simplified manner:

- (1) Additional photolysis increases the source terms for OH and HO_2 and, therefore, their concentrations,
- (2) Higher concentrations of OH more rapidly deplete organic precursors, creating additional ozone in the radical chain oxidation process of photochemical smog,
- (3) Higher OH also removes NO_2 more rapidly, forming HNO_3 ,
- (4) Higher OH and O_3 diminish NO concentrations, eliminating a major sink for HO_2 and allowing it to increase, and
- (5) With little NO_x remaining in the system, HO_2 is lost through radical-radical recombination reactions, forming such products as H_2O_2 .

The plots given in Figure 4-6 are all consistent with this description. For instance, the NO_2 and HNO_3 traces are plotted on the same ordinate scale to point out that the lost NO_2 appears as HNO_3 due to increased reaction of NO_2 with OH at that time of day (OH reaches concentrations as much as three times higher in the 0.200 cm-atm simulations). Also note that the O_3 and HNO_3 traces generally track each other quite well, since both are dependent on OH flux and NO_x concentration changes. As for H_2O_2 sensitivity, consider the differences in the concentrations and timing of the mid-afternoon OH peak, which influences the late-afternoon yields and time offsets for HO_2 (though it is difficult to detect, NO at this time is at least an order of magnitude lower in concentration for the 0.200 cm-atm scenarios), and therefore, the end-of-the-day production rate of H_2O_2 . The result is the shapes and timing of the H_2O_2 curves shown in Figures 4-1 through 4-4. We did not plot H_2O_2 for the Group 4 case (Figure 4-5) because enough NO remained in the air parcel at all times to hold down HO_2 concentrations and, thus, H_2O_2 production.

Philadelphia, PA - 24 June 1980

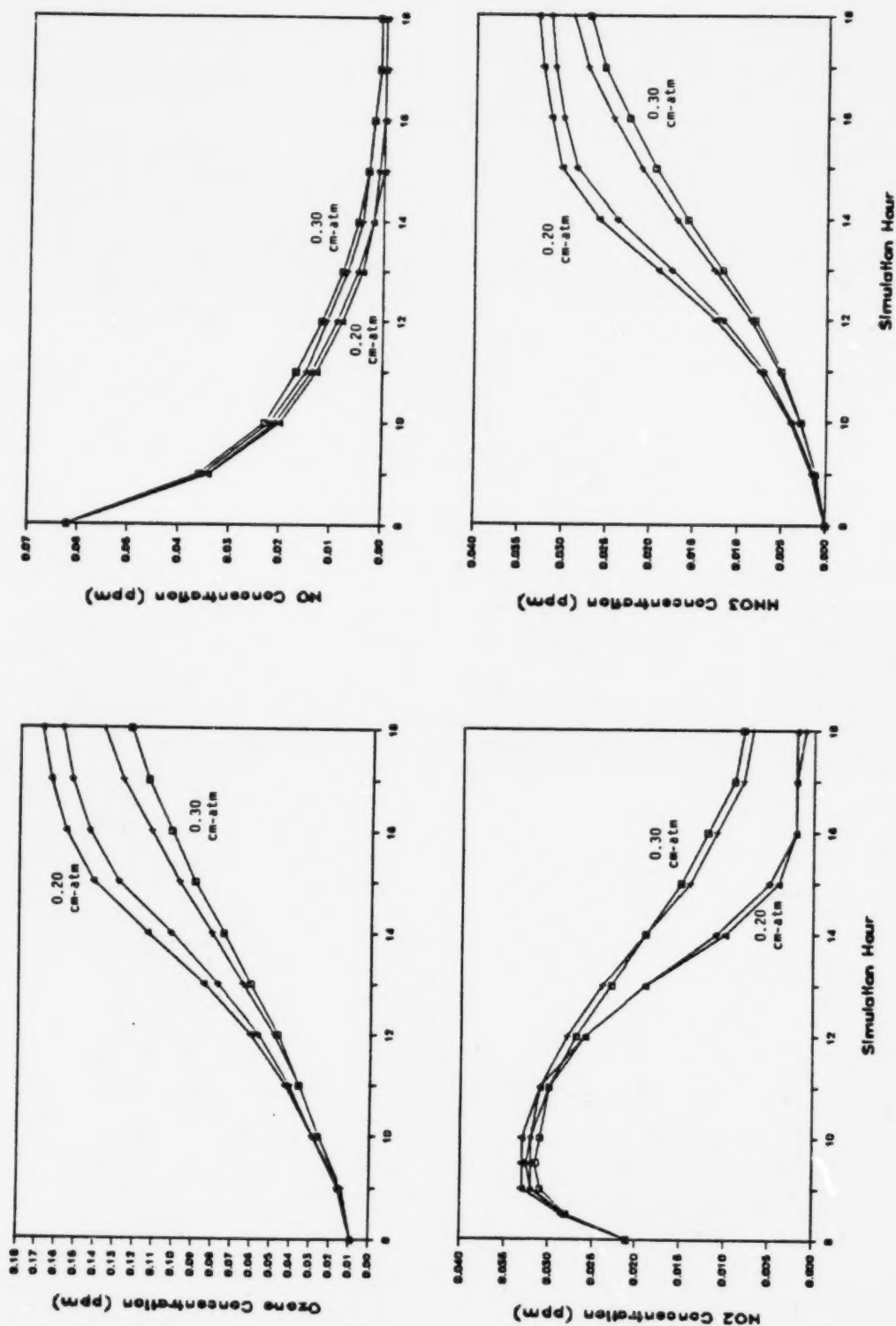


FIGURE 4-6. Ozone, NO₂, NO, and HNO₃ plots for extreme scenarios in the future sensitivity tests-- simulation of 24 June 1980, Philadelphia, Pennsylvania.

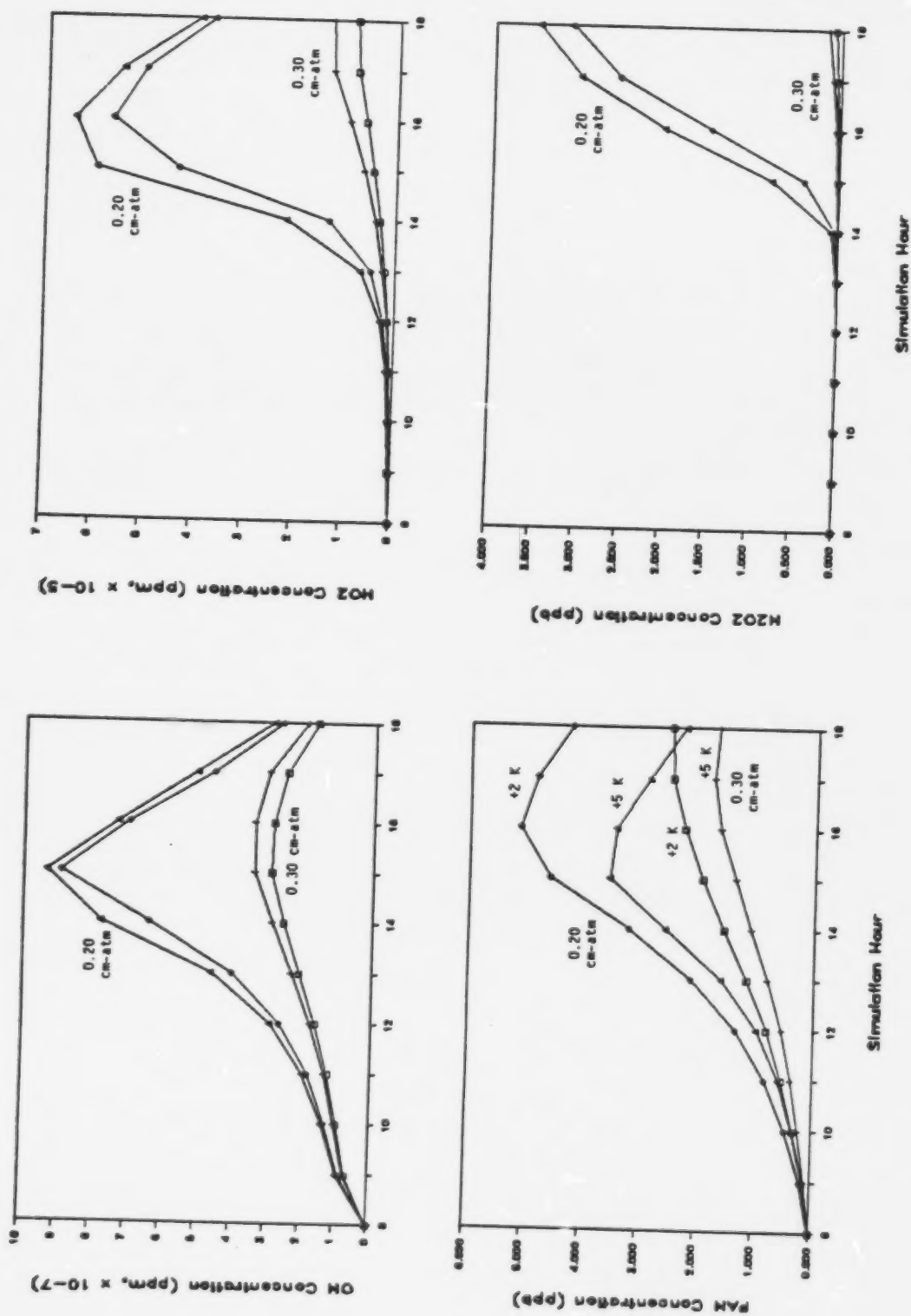


FIGURE 4-6. Concluded.

DISCUSSION OF SINGLE-DAY SCENARIO RESULTS

The previous discussion was intended to provide the reader with an understanding of the photochemical processes occurring at various periods in the future sensitivity scenarios. We now present more complete results from these sensitivity tests. Because the primary objective of this research was to investigate potential impacts of global changes on urban ozone formation, and because our future scenarios were based on control of NMOC to attain the ozone NAAQS, we discuss the predicted responses of ozone concentrations to these global changes in depth. Since urban production of hydrogen peroxide might influence aqueous-phase acidification in downwind areas, we also consider the effects of both future NMOC control and potential global changes on H_2O_2 concentrations. Whenever possible, the previous discussion and figures are referred to. For each species, we first consider the effects of temperature increases, followed by a discussion of the impacts of increased ultraviolet irradiance due to decreases in stratospheric ozone levels. Following our presentation of these data, we address the impacts of combined changes and discuss the implications of future changes.

Ozone

The predicted effects of surface temperature increase for a 0.300 cm-atm overhead ozone column are shown in Figure 4-7. These data represent the percent increases predicted for maximum hourly ozone for +2 and +5 K increases over the base-case temperature profiles. The divisions in the figure represent the first three general test groups previously described. We see from these plots that the average rate of predicted ozone increase per degree Kelvin (over the +5-K range of this study) was nearly linear in these groups. The resulting rates are given in Table 4-1, averaged for each general test group. Rates of increase in that table are calculated from the results of the +5-K simulations. In almost all cases, the rates calculated from the +2-K simulations are statistically indistinguishable from the +5-K simulations, indicating a linear increase over the 5-K degree (9 Fahrenheit degree) range of this study.

It is also possible to estimate the effects of temperature increase for the non-base-case overhead ozone columns (0.250 and 0.200 cm-atm) by determining the relative percentage increase in the ozone maximum over the normal temperature predictions for each ozone column. For instance, though the Los Angeles simulations showed average hourly ozone increases above the future base case of 40.2 percent, 44.6 percent, and 47.3 percent

Percent Increase over Base Case Ozone

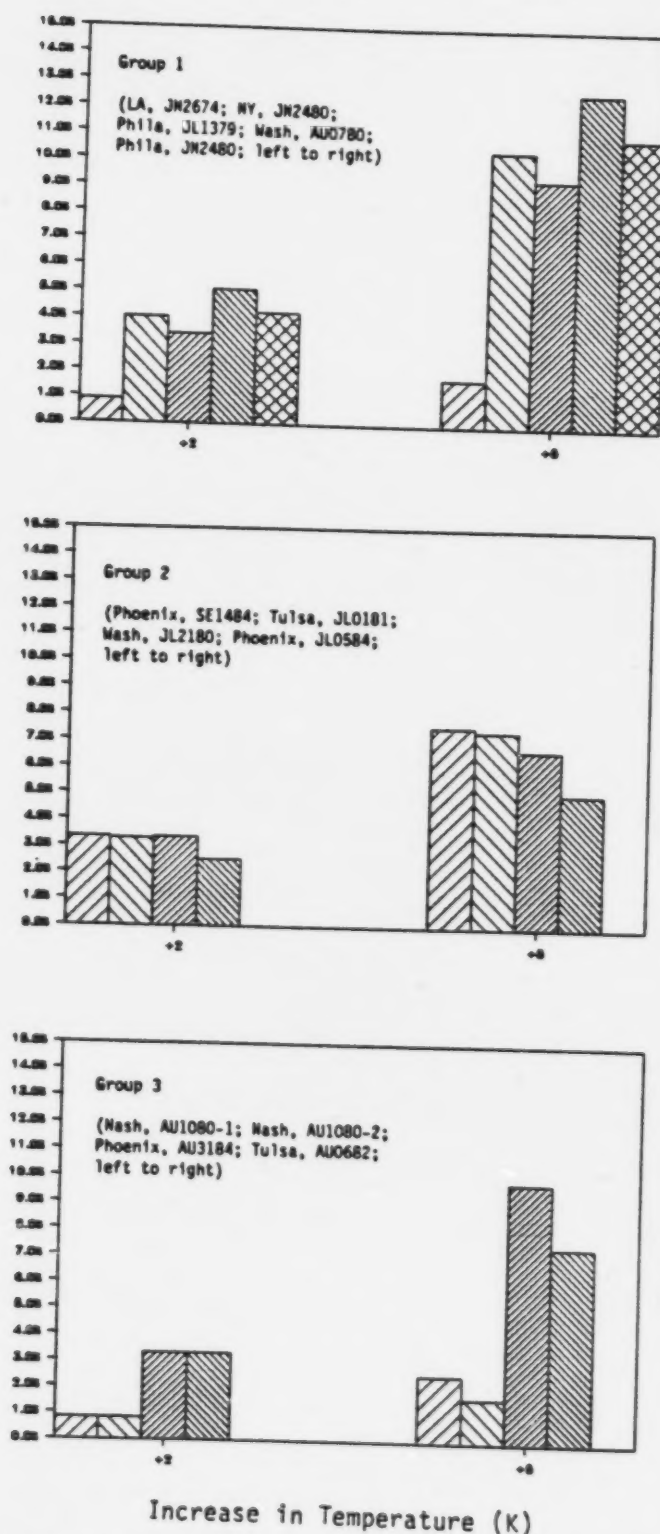


FIGURE 4-7. Percent increase in predicted ozone over the future base case (0.12 ppm) for two temperature increments and three test groups.

for +0 K, +2 K, and +5 K at a 0.200 cm-atm ozone column, the relative increases over +0 K for that column were 3.2 and 5.1 percent for the +2 K and +5 K scenarios. Performing similar calculations for all cities and groups, we find that the 0.300 cm-atm linear factors hold quite well through the 0.250 cm-atm calculations, and begin to diminish only slightly for 0.200 cm-atm (see Table 3-21). As we see later, this is an indication that the higher energy conditions present at 0.200 cm-atm tend to use a large fraction of the oxidant-forming potential of these urban systems (especially in the more reactive, Group 1 test cases), leading to diminished ozone formation potential in the more extreme cases. Note also that though the potential to form more ozone with increased temperature is diminished, it is still a positive response.

As previously discussed, the Group 4 scenarios represent a somewhat unique set of conditions compared to those of the other three general groups because of their singular location, meteorological, and initial concentration conditions. As noted, these conditions cause significant differences in future reactivity because of the greater sensitivity of the air parcels to increased ultraviolet or thermal energies of the future conditions. For the base-case ozone column simulations, a 2.6 percent/K increase was detected over the 5-K range of the study. Relative increases calculated for the smaller ozone columns indicate an increasing ability to produce ozone with decreasing ozone column (i.e., there is no evidence of diminished ozone-forming potential over the ozone column range of this study as there was in the other groups). We provide these results in Table 4-1 and because of the unique character of these simulations, we also list overall average results with and without the Group 4 data. Predicted overall average increases in maximum hourly ozone due to increased surface temperature are 1.6 percent/K (including the data from Group 4), or 1.4 percent/K (2.5 percent/degree Fahrenheit) for only the first three groups. The latter value decreases to 1.2 percent/K for the 0.200 cm-atm overhead ozone column simulations.

A comparison of the concentration traces used to represent each general test group (Figures 4-1 through 4-6) indicates sensitivity to potential increases in ultraviolet irradiation (ozone column depletion) in all tests. However, these results also indicate that though the amount of time required to produce concentrations near the NAAQS is clearly shortened, the maximum predicted ozone does not always increase significantly. Therefore, we focus next on the predicted effects of ozone column depletion on maximum hourly ozone concentrations, as shown in Figure 3-26 for the first three general test groups. Recall that the Group 1 and 4 future base case scenarios showed increasing ozone concentrations at the 1800 hour termination of EKMA and individual scenario calculations, indicating that those systems had not yet reached their individual oxidant-forming potential. Additional input of thermal or radiant energy into

Table 4-1. Rates of Increases in Maximum Hourly Ozone Concentrations with Increases in Temperature and Decreases in Overhaed Ozone Column¹

Ozone Column:	<u>Average O₃ Increase (percent/Kelvin)</u>		
	<u>0.30 cm-atm</u>	<u>0.25 cm-atm</u>	<u>0.20 cm-atm</u>
<u>Test Group</u>			
1	1.8	1.9	1.4
2	1.3	1.2	1.2
3	1.1	0.9	0.9
4	(2.6)	(3.0)	(3.5)
Total (1,2,3)	1.4	1.4	1.2
Total (all)	1.6	1.6	1.5

Temperature:	<u>Average O₃ Increase (pct./pct. decrease in O₃ column)</u>		
	<u>base</u>	<u>base + 2 K</u>	<u>base + 5 K</u>
<u>Test Group</u>			
1	1.1	1.1	1.0
2	0.1	0.1	0.1
3	-0.1	-0.1	-0.1
4	(1.4)	(1.5)	(1.6)
Total (1,2,3)	0.4	0.4	0.4
Total (all)	0.5	0.5	0.5

¹Percent increases are increases over the future base case value of 0.12 ppm.

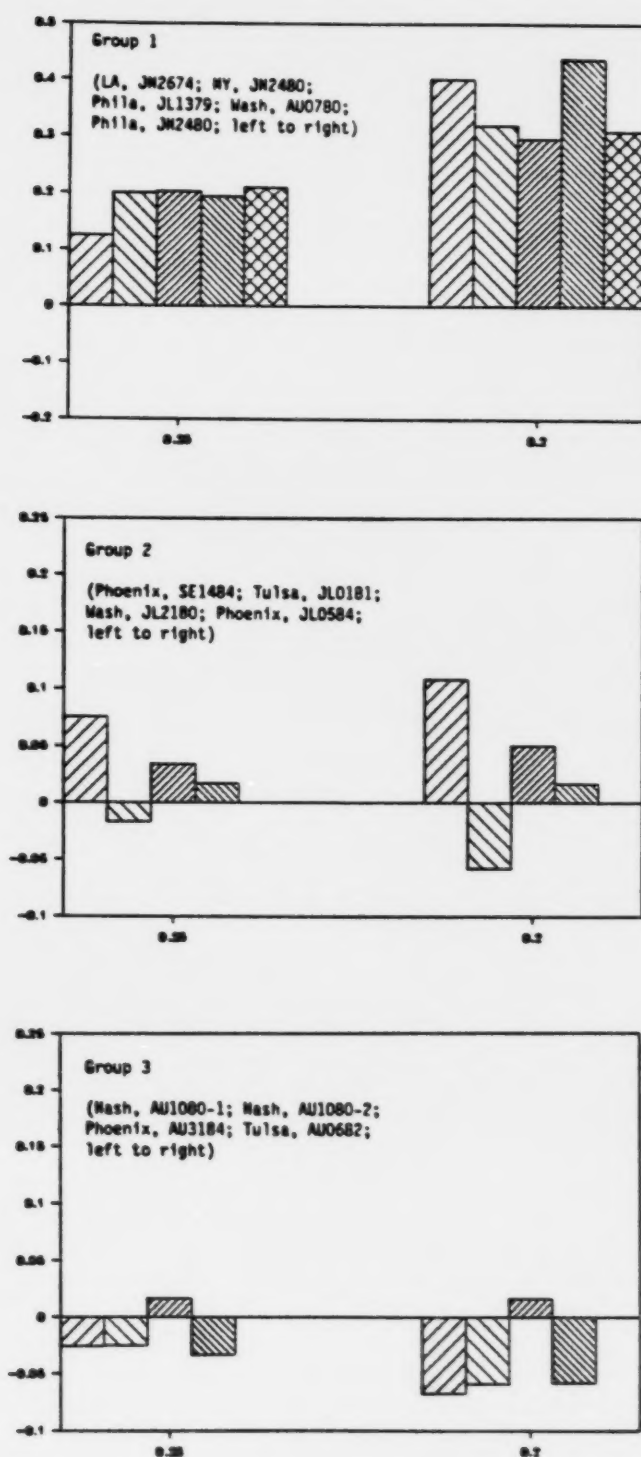
these systems due to future global changes was predicted to enhance reactivity and result in greater production of ozone and other oxidation products prior to 1800 hours. These results are summarized in Table 4-1 and indicate that approximately a 1.0 percent increase in surface ozone maximum concentration was predicted for each percent decrease in overhead ozone column. For Group 4, this value was about 1.4 percent; as with the temperature data, this rate increased with additional depletion of the column. The less reactive groups (2 and 3) yield only a 0.1 and -0.1 percent change in ozone for a percent change in overhead column (note the ordinate scale change in Figure 4-8), indicating that most or all of the future scenario oxidant-forming potential had already been achieved in the base-case simulations. The results for these groups (and Group 1) were generally linear over the 0.10 cm-atm range of study, though slightly higher rates of change were found in the 0.30 to 0.25 cm-atm comparisons than in those from 0.25 to 0.20 cm-atm. Therefore, in almost all cases, additional energy input from the future scenarios produced ozone at or above the ozone NAAQS (the future base case), and always produced ozone and other oxidized products faster (sometimes hours faster) than the base case simulations.

Hydrogen Peroxide and Other Products

The hydrogen peroxide results are not easily described for two reasons: First, as noted in the photochemical dynamics discussion, H_2O_2 production rates and concentrations are extremely sensitive to variations in radical flux. In addition, since radical flux is a function of ultraviolet irradiance, the increases in H_2O_2 are linked to decreases in stratospheric ozone. This is especially obvious when contrasted with ozone changes since, unlike ozone, H_2O_2 does not have a significant photolysis loss reaction. Therefore, once chemical conditions are such that H_2O_2 buildup begins in the afternoon, there are only minor H_2O_2 loss reactions to suppress concentration increases (which are usually only halted at sunset when radical concentrations drop substantially).

The second reason why the predicted impact of future global changes on urban H_2O_2 concentrations is less easily described is that there is no simple standard reference concentration on which to base a reasonable comparison. The individual simulation results given in Tables 3-6 through 3-20 present percentage increases of predicted future values over those of the future base case (+0 K/0.300 cm-atm) simulation. For ozone, such comparisons are very pertinent because of the federal mandate to achieve future base case conditions (0.12 ppm), which is the basis of the protocol that directs this study. There is, however, no such common basis for

Percent Increase over Base Case Ozone



Future Ozone Column Density (cm-atm)

FIGURE 4-8. Percent increase in predicted ozone over the future base case (0.12 ppm) for two ozone column density decrements and three test groups.

hydrogen peroxide comparisons. In addition, because the NMOC emission controls used in our EKMA calculations to derive future base-case conditions appear to be very effective in the limitation of hydrogen peroxide formation, relative comparisons of increases in H_2O_2 concentration over the future base-case values (Tables 3-6 through 3-20) can yield huge percentages. These numbers are derived from photochemical kinetics model predictions indicating that the effect of NMOC controls should tend to limit the photochemical reactivity in an air parcel, shifting the oxidant-formation period to later in the afternoon when the solar irradiance is diminishing. Hence, the oxidant-formation potential is not completely reached, NO_x is not as completely consumed; and a significant HO_2 sink (NO) still remains to hold the concentration (the source of H_2O_2) in check.

Because there is currently no hydrogen peroxide NAAQS and the future base-case concentrations provided in Tables 3-6 through 3-20 are not fixed concentrations (but rather very low values resulting from the large benefit of NMOC emission control), we briefly summarize the predicted increases in H_2O_2 concentrations above these future base-case concentrations. In effect, this is an estimate of the potential "disbenefit" resulting from future global changes) after control of NMOC to attain the ozone NAAQS. In addition to this measure, however, we also compare the predicted future case H_2O_2 concentrations against the original (pre-NMOC-control) base-case H_2O_2 prediction for the conditions of each data set. In this way, we can at least describe the relative changes from present to future conditions, by combining expected future NMOC controls and potential future global changes.

As we have shown in our discussion of urban photochemical processes, the changes in maximum hydrogen peroxide concentrations due to increases in surface temperature are rather insignificant compared to the effects predicted as a result of increases in ultraviolet intensity. Table 4-2 indicates that the relative rates of increase over the H_2O_2 concentrations attained with NMOC control (to meet the NAAQS for ozone) are moderate compared to the relative H_2O_2 increases resulting from a one percent decrease in ozone column. This comparison becomes even more exaggerated if we roughly estimate that the likelihood of a +2-K increase is approximately similar to a 10 percent decrease in the ozone column. This indicates that loss of the benefit of NMOC controls will probably only occur with future increases in radiant energy.

A comparison of the predicted H_2O_2 concentrations to the original base-case concentrations, however, more clearly points out the initial benefits of future NMOC control, and the resulting "disbenefit" caused by these changes in future conditions. Table 4-3 shows the relative differences

Table 4-2. "Disbenefit" to Future Base Case Maximum Hourly H_2O_2 Concentrations Caused by Increases in Temperature and Decreases in Overhaed Ozone Column¹.

<u>Average H_2O_2 Increase (percent/Kelvin)</u>			
Ozone Column:	<u>0.30 cm-atm</u>	<u>0.25 cm-atm</u>	<u>0.20 cm-atm</u>
<u>Test Group</u>			
1	15.6	17.5	6.0
2	3.8	1.5	0.4
3	1.4	0.6	0.2
Total	6.9	6.5	2.5

<u>Average H_2O_2 Increase (pct./pct. decrease in O_3 column)</u>			
Temperature:	<u>base</u>	<u>base + 2 K</u>	<u>base + 5 K</u>
<u>Test Group</u>			
1	158.0	133.8	108.0
2	7.2	6.4	5.5
3	2.9	2.8	2.5
Total	56.1	47.7	38.7

¹Percent increases shown are increases over the H_2O_2 concentration after NMOC control to achieve the ozone NAAQS. Typically, these base values are very low indicating a significant benefit from NMOC control. Los Angeles and Seattle base case H_2O_2 data were less than 0.01 ppb. Percentage increases over these concentrations were not included in these calculations.

Table 4-3. Comparisons of Future Scenario Maximum Hourly H₂O₂ Concentrations versus Original Base Case H₂O₂.

	<u>H₂O₂ Difference / Original H₂O₂ at base Temperature</u>		
Ozone Column:	<u>0.30 cm-atm</u>	<u>0.25 cm-atm</u>	<u>0.20 cm-atm</u>
<u>Test Group</u>			
1	- 95.6	- 57.4	123.8
2	- 60.4	- 30.4	12.4
3	- 30.5	- 2.4	28.8
Total	- 62.2	- 30.1	55.0

	<u>H₂O₂ Difference / Original H₂O₂ at base Temperature +2 Kelvin</u>		
Ozone Column:	<u>0.30 cm-atm</u>	<u>0.25 cm-atm</u>	<u>0.20 cm-atm</u>
<u>Test Group</u>			
1	- 94.3	- 47.4	139.6
2	- 58.3	- 28.4	13.5
3	- 29.5	- 1.9	29.6
Total	- 60.7	- 25.9	60.9

	<u>H₂O₂ Difference / Original H₂O₂ at base Temperature +5 Kelvin</u>		
Ozone Column:	<u>0.30 cm-atm</u>	<u>0.25 cm-atm</u>	<u>0.20 cm-atm</u>
<u>Test Group</u>			
1	- 91.7	- 31.2	158.9
2	- 55.2	- 25.9	14.9
3	- 27.5	- 0.4	29.8
Total	- 58.1	- 19.2	67.8

between predicted future and original H_2O_2 concentrations. Three sets of data representing the changes due to decreases in the ozone column for different temperature profiles are shown. As noted, these data sets are very similar, indicating the relative insensitivity to temperature increases. The main point to be drawn from these data is that until the ozone column decreases to 0.25 cm-atm (a 16.7 percent decrease), the NMOC control applied to derive the future base case of ozone compliance is predicted to also control H_2O_2 to below its original level. In all cases, however, the positive values in Table 4-3 for the 0.20 cm-atm simulations indicate that these test air parcels have significant potential to produce greater amounts of H_2O_2 than predicted for the original air parcel using original, uncontrolled NMOC emissions. As noted, this is caused by the additional radiant energy input, which causes higher radical fluxes and more rapid depletion of NO_x , providing afternoon conditions more conducive to hydrogen peroxide formation.

Synergistic Effects

This discussion has so far attempted to delineate isolated impacts on future urban air parcels resulting from global changes. We can also analyze the available data for an indication of whether synergistic effects are predicted to occur. On the basis of the generally linear decreasing rates of impact resulting from increases in ultraviolet intensity and surface temperatures, we conclude that the combined effect of increases in these parameters appears to be sometimes additive, but not synergistic within the range of conditions simulated. Such a finding is entirely consistent with our description of urban photochemical processes, assuming that there is a limit to the oxidizing potential of a polluted air mass. Thus, even though the short-term production rate of ozone and other oxidized species is often enhanced by both an increase in temperature and ultraviolet intensity, the long-term effect of combining these two energy sources is, at best, additive because there are only limited amounts of oxidant precursors available.

Summary of Single-Day Results

In summarizing city-specific simulation results, we recall that our original intent in selecting the non-base-case, future temperature and overhead ozone column values was to investigate whether unanticipated changes in surface temperature or stratospheric ozone levels could cause additional ozone production in urban areas that had achieved the NAAQS for ozone through NMOC emission control. We selected two different ranges of change for both the temperature and ultraviolet irradiation levels, and analyzed

model results for different combinations of these parameters. Temperatures that were 2 K above the base-case temperature profiles and an overhead ozone column of 0.250 cm-atm were selected as a moderate or probable (based on the best estimates available in the literature) future scenario. More extreme conditions of +5 K and 0.200 cm-atm were also selected to provide large, but not unrealistic, changes. We provide the average group changes for predicted maximum hourly ozone concentration under these conditions in Table 4-4 as a general summary of these results.

As we have stated throughout the previous discussion, the highly reactive air parcels from the Group 1 cities do not appear to be able to easily sustain the ozone NAAQS level of 0.120 ppm under any conditions of increased future energy input. Much of this sensitivity stems from the fact that the EKMA calculations (and therefore, our future scenario base cases), which are used to determine the amount of necessary NMOC reductions, end at 1800 hours when the ozone concentration is still increasing. This provides increased oxidant-formation potential in the form of extra, "allowed" NMOC emissions, which are more effectively used in the future scenarios because those conditions are more reactive. For moderate changes in the future temperature and ozone column parameters, an unanticipated extra ozone production of 0.024 ppm, or 23.3 percent is predicted, on the average, for these very reactive days. More extreme conditions could result in additional ozone formation, with an average Group 1 ozone concentration of 0.174 ppm predicted for EKMA-derived NMOC controls under the most extreme conditions.

Future scenario results from the two less reactive groups appear to indicate that in those cases where nearly the full oxidant-formation potential was realized and controlled by the EKMA-derived NMOC controls, only small or no increases in the hourly maximum ozone concentration might be expected for even the more extreme future conditions. On the other hand, it must be kept in mind that the time required to achieve these daily maximum concentrations is shortened by the additional energy input. This, in turn, could result in extra cumulative human exposure even though the maximum concentration changes little.

Finally, for the the Group 4 data, we obtained simulation results that, if verified by future measurements and modeling studies, would provide a different set of conditions, also very sensitive to future changes in temperature and ozone column density. The EKMA calculations for these data sets required little NMOC control because high NO_x conditions were combined with the lower light intensity of northern locations and unique mixing depth conditions. However, when the light intensity was increased to account for less stratospheric ozone absorption, these same conditions led to a highly reactive, poorly diluted, precursor-rich air parcel that

was capable of producing high levels of ozone and oxidized products (see Table 4-4). Although these data and simulations need to be verified, it is interesting to note that the ozone traces from the base-case simulations were similar to the Group 1 results, in which concentrations were still increasing at the end of the EKMA calculation (1800 hours). However, unlike the Group 1 simulations, where the system's oxidant-forming potential might have been nearly reached in one or two more hours of simulation, it is unlikely that this would have occurred before sunset in the Group 4 data sets. Therefore, in these situations, there does not even appear to be a simple method of estimating (or justifying) the amount of additional NMOC reduction that would be needed to curtail such unanticipated formation of ozone.

The city-specific simulation results for H_2O_2 production are somewhat more reassuring. These simulations indicate that in all cases studied, H_2O_2 production is far more sensitive to varied NMOC and ultraviolet radiation conditions than is ozone predictions. That is to say, reduction of H_2O_2 to concentrations far below the original values was effectively performed through reduction of NMOC emissions as prescribed to achieve the NAAQS for ozone. On the other hand, the loss of this benefit was rapid with decreasing overhead ozone column. The most sensitive test cases were the most reactive Group 1 sets that required the highest NMOC controls. However, in almost all cities, a 16.7 percent decrease in ozone column density still resulted in the production of less H_2O_2 than in the original base-case simulation. At smaller ozone columns, more rapid increases were predicted, depending on the overall reactivity of the specific test group (see Table 4-3), to concentrations greater than the original H_2O_2 concentrations.

DISCUSSION OF MULTI-DAY RESULTS

The chemical processes that occur for the multi-day simulations do not differ greatly from those of the single-day simulations, though one may have a different perspective when viewing a multi-day event. The results of the Phoenix simulations are shown in Figure 4-9. Whereas earlier plots showed the four extreme scenarios of temperature and overhead ozone column density, these plots and the following set of Los Angeles plots show the base-case, moderate, and extreme combinations of test conditions. A comparison of these figures shows that enough (NO_x) emissions occur later in the day to continue ozone production throughout the afternoon, yielding the maximum hourly concentration at 1900 hours in all cases. The potential global climate changes represented by the future scenarios conditions increased the maximum predicted ozone concentration of 0.100 ppm (base case) to 0.123 ppm for the most extreme future conditions (+5 K/0.200 cm-atm). This is an interesting consequence of the Phoenix data set used, in

Table 4-4. Group Averaged Ozone Responses to Moderate (+2 Kelvin/0.25 cm-atm) and Extreme (+5 Kelvin/0.20 cm-atm) Changes to Future Scenario Conditions.

Scenario:	<u>Percent Ozone Increase</u>		<u>Calculated Ozone (ppm)</u>		
	<u>Moderate</u>	<u>Extreme</u>	<u>Base</u>	<u>Moderate</u>	<u>Extreme</u>
<u>Test Group</u>					
1	23.3	45.1	0.120	0.148	0.174
2	5.4	9.0	0.120	0.126	0.131
3	0.4	0.4	0.120	0.120	0.120
(4)	(24.9)	(72.1)	0.120	0.150	0.207
Total (1,2,3)	10.8	20.2	0.120	0.133	0.144
Total (all)	(12.6)	(27.1)	0.120	0.135	0.153

Phoenix, AZ - Compliance Day

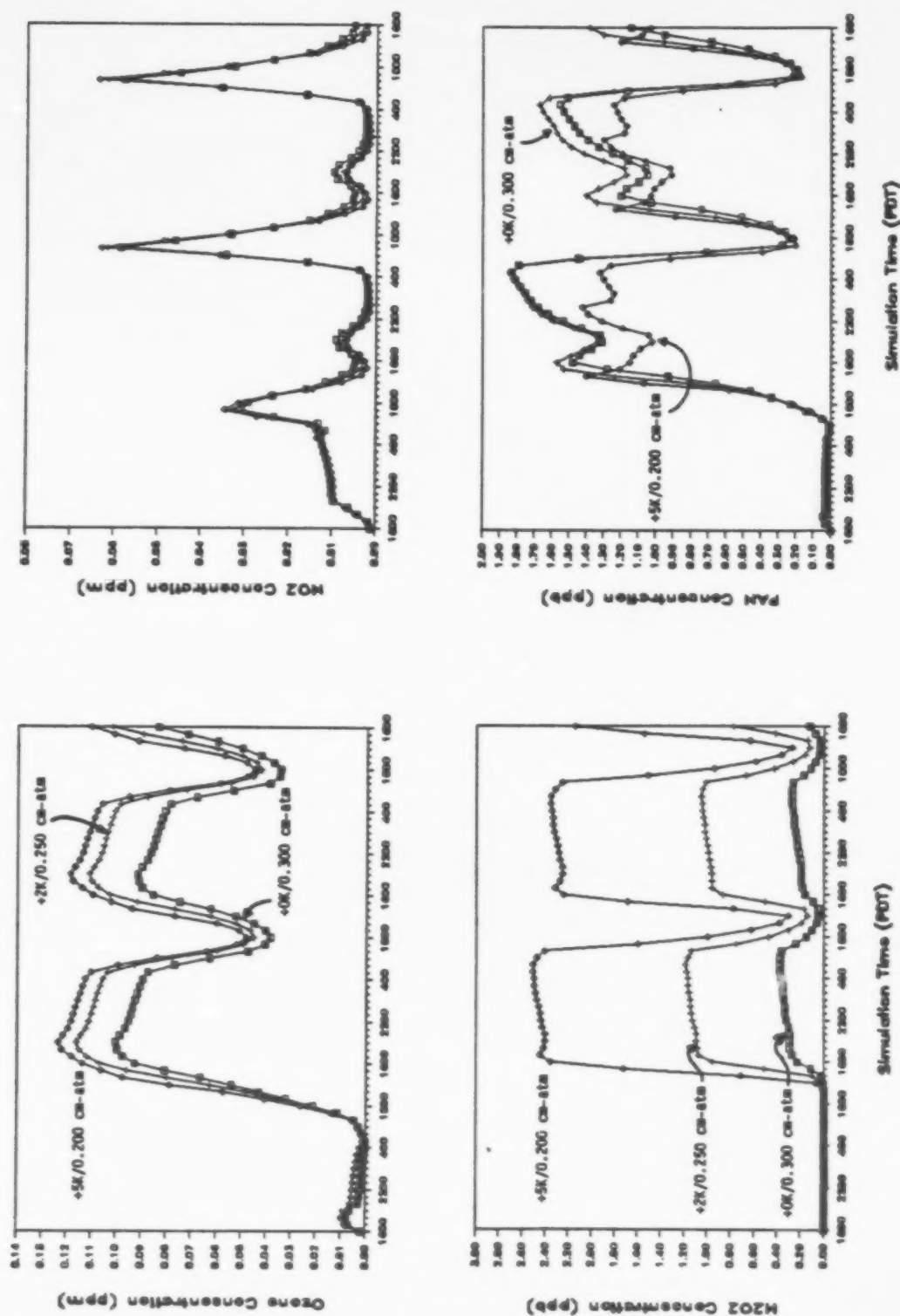


FIGURE 4-9. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests-- multi-day simulation of an ozone NAAQS attainment scenario for Phoenix, Arizona.

that afternoon NO_x and VOC emissions provide a higher oxidant-forming potential because they occur during a key ozone-forming period. Not all data for the Group 2 and 3 city-specific scenarios had such emissions data available for that time of day. This lack of emissions data could artificially reduce the calculated oxidant forming potential for those test cases.

Other predicted impacts of the potential future scenarios are as might be expected from the single-day discussion. The maximum hydrogen peroxide concentrations increased by nearly a factor of 10 between base case and extreme conditions. This is as expected since the increased radiant energy prolongs the afternoon period when H_2O_2 production is viable. PAN concentrations also decrease with increasing temperatures; this was seen in the single-day results and is explained by the extreme temperature-dependency of the PAN decomposition reaction. In all scenarios, the hourly emissions profile can be detected in the NO_2 plot, though the ozone "left over" after the first and second days of simulation tends to reduce NO_2 levels during the second and third nights, and increase the NO_2 levels on the second and third mornings by converting emitted NO to NO_2 . Other than these commonly seen, second-day effects, little difference is apparent from day to day for any of the future condition test sets. However, this is not the case for the Los Angeles simulations.

The results of the multi-day Los Angeles simulations are shown in Figure 4-10. These days follow trends similar to those just described, but we also see the effect of the unique characteristics of the Los Angeles Basin. Two very different sets of parameters for the Los Angeles and Phoenix multi-day simulations are the mixing height and emission profiles. Whereas the Los Angeles data set provides very high emissions into a relatively poorly diluted air parcel, the Phoenix attainment simulation has rather low emissions with a large increase in mixing height throughout the day. Of course, these multi-day profiles assume that the air parcels have not been transported outside the urban area, and therefore are impacted by similar emissions and mixing depths on each day. For the Los Angeles simulations, these conditions result in increasing ozone and oxidized product yields for each successive day.

Unlike the Phoenix attainment simulations, future Los Angeles scenarios show interesting and different multi-day effects for the proposed global conditions. In the single-day Los Angeles simulations, H_2O_2 concentrations were predicted to be so low for the future base case simulation that percent increases could not be calculated. This is again true for the first day of the multi-day future tests (since it is the same simulation for that period), but interesting differences begin to develop as the

Los Angeles, CA - 26-27 June 1974

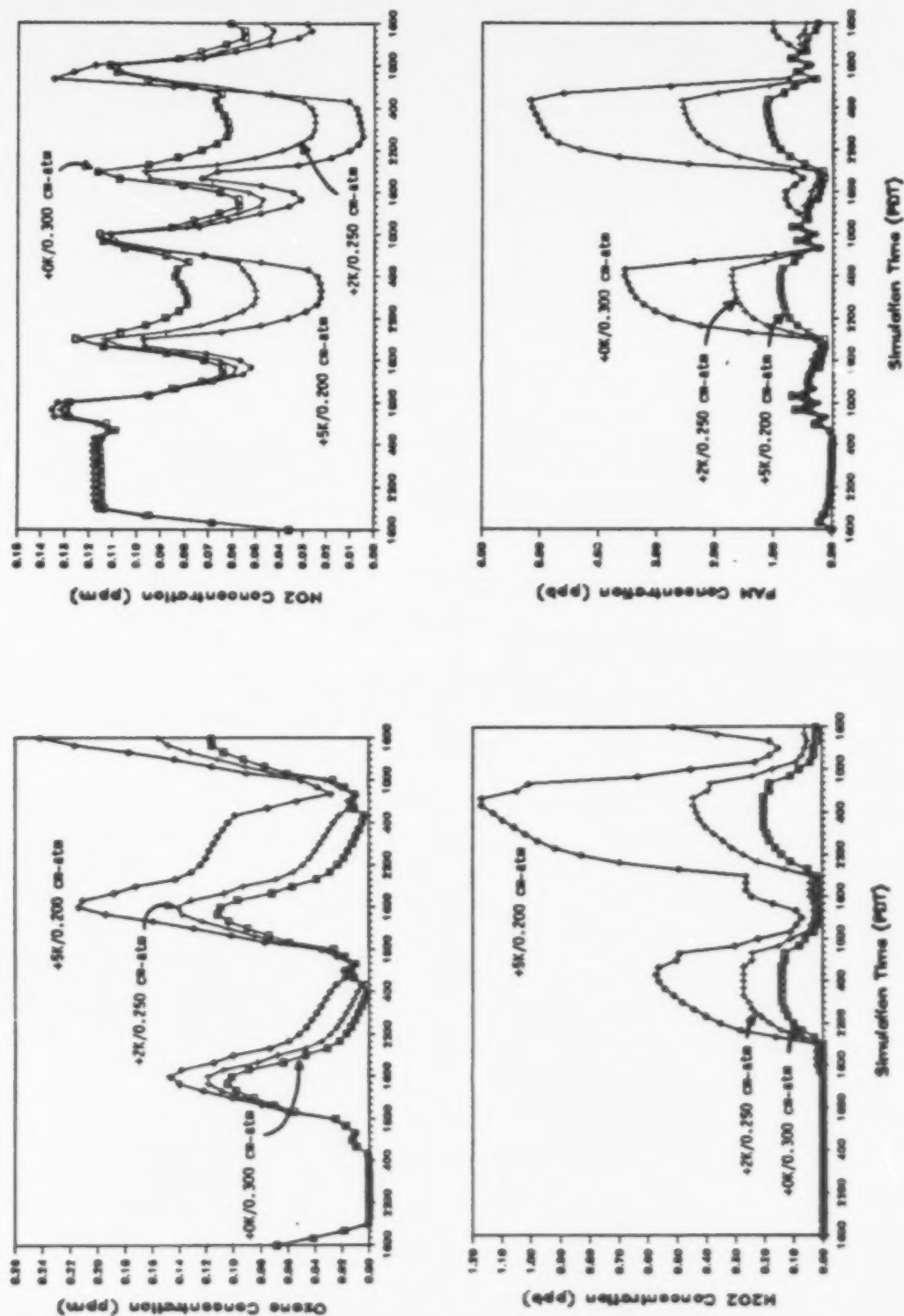


FIGURE 4-10. Ozone, NO₂, H₂O₂, and PAN plots for extreme scenarios in the future sensitivity tests-- multi-day simulation of 26-27 June 1974, Los Angeles, California.

second- and third-day concentrations begin to vary between scenarios. The reason H_2O_2 concentrations are low in the late afternoon is that NO_x emissions and concentrations are large enough to hold hydroperoxy radical concentrations to low values. As conditions change and ozone concentrations build significantly, NO_x is titrated by the ozone and the hydroperoxy radical (and its combination product hydrogen peroxide) increases in concentration rapidly. These trends are apparent in both the ozone and NO_2 traces for the second and third nights. For the most extreme future conditions, the model predicts ozone concentrations nearly at the standard prior to sunrise of the third day. The corresponding high nighttime values resulted in very low NO_2 concentrations and NO levels approaching zero. The model predicts that these conditions allow HO_2 radicals to be produced, even at night, to concentrations that allow H_2O_2 buildup. The primary source appears to be the reaction of ozone with available VOC, which also produces peroxyacetyl radicals, the source of increasing PAN. Extreme conditions also yield ozone concentrations of about 0.25 ppm by the third day (as opposed to about 0.11 ppm for the base case). This amplification of photochemical oxidant formation appears to be due to the ability of the higher radiant and thermal energy conditions in the extreme future scenario case to more efficiently convert the ample Los Angeles precursors to oxidized products. Of course, this effect is maximized by our assumption that the air parcel remain in the Los Angeles Basin for three days.

DISCUSSION OF ALTERNATE MECHANISM SIMULATIONS

The alternate (CALL) mechanism was used in this study only to verify that simulation results were not due completely to mechanism singularities. We selected two different test cases with which to perform this test. The CALL mechanism results are provided for nine future scenarios for the test days of 5 July 1984 in Phoenix and 13 July 1979 in Philadelphia (Tables 3-23 and 3-24). These results can be compared with the CBM-X results already provided in Tables 3-14 and 3-8, respectively. We note that the maximum hourly ozone predicted for the Phoenix day was little affected by the future changes in either mechanism, and that H_2O_2 and PAN concentrations tracked well between mechanisms in both magnitude and percent change.

The Philadelphia test was a Group 1 day and, therefore, more sensitive to the proposed future global changes. The comparison of the results of the mechanisms for this test points out some differences. In a very cursory fashion, we note some of these differences in the PAN and radical-radical chemical reactions. We see, for instance, that the CALL mechanism generates more PAN and less H_2O_2 than the CBM-X. On the other hand, the base-case and moderate ozone predictions are almost identical, with CBM-X predicting slightly less than CALL for extreme conditions. Since these mechanisms are primarily evaluated for ozone prediction capabilities, it is

not suprising that those predictions are closer than the H_2O_2 and PAN concentrations. In addition, though this is only one test of the more reactive systems, we perceive it as some evidence that (1) the project results are not mechanism artifacts, and (2) the CBM-X mechanism could prove to be slightly conservative in its predictions compared to the newer CALL and CBM-IV mechanisms.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

This report describes the investigation of two specific, but related, topics. The goal of this work was to evaluate the potential impacts of future (1) decreases in stratospheric ozone concentrations and (2) increases in surface temperature on urban photochemical systems. Although most photochemical kinetics models allow direct input of temperature values, it is necessary to convert the projected values for overhead ozone column density into parametric representations such as photolysis rates. Therefore, the first task was to assess the data and methodologies currently available for calculating the photolysis rates used in air quality simulation models. From this assessment, we determined the appropriate data and numerical algorithms to describe these relationships. Following these determinations, we began the second task, which was to calculate the variation (with ozone column density) in photolysis rates, and, in combination with assumed temperature variations, to use these values to determine the sensitivity of urban atmospheres to global changes in these parameters. This sensitivity evaluation consisted of analyzing the impact that these increases in thermal and radiant energy input might have on the chemistry of future urban air parcels. In the following subsection we summarize separately the conclusions of these two tasks, followed by recommendations derived from these conclusions.

ASSESSMENT OF PHOTOLYTIC RATE CALCULATIONS

In this phase of the work, we focused on the ultraviolet photolysis of ozone [to $O(^1D)$] and formaldehyde since these are the most significant, radical-generating photolysis reactions in the troposphere; thus, their associated uncertainty translates almost directly into uncertainty concerning the radical production rate of polluted air masses. We also identified data and algorithms we felt to be potentially useful in the development of a new generation of ultraviolet actinic flux calculation schemes for current and developing models. Our predictions were then compared with actual measurements and the uncertainty associated with each step of the process was examined. Because the calculation of atmospheric

photolysis rates is the product of actinic flux and specific molecular properties integrated over wavelength, we addressed three separate areas: (1) the methods and data needed to calculate actinic flux, (2) uncertainties in experimentally derived values for molecular properties, and (3), the integration approach and related uncertainties.

The first of these three areas was the most difficult to assess because the calculation of actinic flux for differing conditions and locations requires consideration of a wide range of complex atmospheric interactions. The most rigorous attempt at this complex description is the work of Braslau and Dave (1973a and b). Demerjian and coworkers (1980) later used a somewhat simplified version of this model to generate a number of actinic flux data sets for various conditions. These data sets have been used extensively over the last decade in almost all photochemical modeling studies of tropospheric air masses. We believe that an update of this work is now in order, if for no other reason than to include more recent extraterrestrial flux data in these calculations, and to provide actinic flux results for conditions not addressed in the original work (e.g., variable ozone column densities), but which are now becoming more important. These new calculations must also be carried out at smaller integration intervals to provide flux data resolved to a magnitude comparable with that of molecular data, so that mathematical averaging errors in the photolysis rate calculations can be limited. This new data would also be very useful in improving the mathematical formulations that are used to estimate actinic fluxes for conditions not directly included in the data (e.g., those of Schippnick and Green, 1982).

Our analysis of molecular data focused on the short wavelength photolysis reactions of ozone and formaldehyde. The greatest individual area of uncertainty in those reactions is found in the absorption cross-section formaldehyde data. Two studies in this area (Bass, 1980; Moortgat, 1979) obtained results that differed by about 30 percent. Since formaldehyde is a very important photolytic species in the troposphere, these numbers translate into a large uncertainty in the radical production capacity of organic oxidation products. We believe that this discrepancy should be alleviated, either through reevaluation of existing data sets or through additional experimental work to develop more data. Absorption cross-section and quantum yield data for ozone are less uncertain, primarily because they have been the objects of experimental investigation for a longer period of time. A somewhat larger associated error develops for ozone photolysis to form $O(^1D)$, however, because this process occurs at the surface ultraviolet cutoff, where actinic flux calculations are less certain. An experimental program designed to measure surface flux distributions in the middle ultraviolet range (particularly in the region near the solar cutoff) would provide information with which the error of J_{010}

calculations might be diminished, and could also yield important data for evaluating and improving actinic flux calculation schemes.

We also investigated the methodology involved in calculating photolysis rates. In cases where two or more of the product terms (actinic flux, quantum yield, and absorption cross section) were highly wavelength-resolved, errors resulted if the wavelength intervals used in numerical integration were much larger than the significant resolved features in the individual functions. This averaging error was only on the order of ten percent, but could be easily eliminated if calculations were performed at 1 or 2 nm intervals. Again, this finding points to the need for a new set of more highly resolved actinic flux calculations, performed in the manner of Demerjian and coworkers (1980).

We believe that the current actinic flux, absorption cross section, and quantum yield data sets result in calculations of ozone [to form $O(^1D)$] and formaldehyde photolysis rates within an uncertainty of about 50 percent. These are the most important photolysis rates in the modeling of tropospheric photochemistry, and more confidence in model results would be gained if this uncertainty could be limited.

EVALUATION OF THE IMPACTS OF GLOBAL CHANGES ON TROPOSPHERIC PHOTOCHEMISTRY

This phase of the report focused on simulating the photochemistry of urban air parcels and evaluating the effects of potential future changes in ozone column density and surface temperature. Because these changes are expected to occur in the future (within a few decades), when many cities would ideally have attained compliance with the ozone NAAQS through reduction of NMOC emissions, we utilized existing information from 1982 and 1987 State Implementation Plans to formulate future scenarios of ozone NAAQS attainment. These scenarios were based on the ideal performance of the EKMA calculations, providing future inputs that resulted in the production of ozone at or below the standard for base-case conditions. The future data sets were carefully developed and screened for errors and to represent as many different cities and general types of original non-attainment situations as possible.

Fifteen future test cases were obtained. For discussion purposes, these were grouped into four general categories based on original ozone production: (1) high non-attainment days with ozone concentrations greater than 0.17 ppm, (2) moderate non-attainment days with original ozone levels

between 0.14 and 0.17 ppm, (3) near-attainment days with ozone concentrations below 0.14 ppm, and (4), a special set of data with unique conditions based on a somewhat uncertain data set from a 1981 Seattle measurement program. The first group was a collection of high ozone production days from Northeast Corridor cities and Los Angeles. Test cases of the second group were from a number of differing cities, thought to have fewer emissions and more beneficial meteorological scenarios than the first group; the third group had even more beneficial conditions.

The changes in photochemical dynamic processes that could be caused by potential global changes in stratospheric ozone and surface temperature have been explained earlier. However, some general concepts and the specific numerical results that evolve from these processes are summarized here. Of primary importance to the impact that future temperature increases or ozone column decreases might have on an urban system is the method by which the additional energy associated with those changes is input into that system. Increased surface ultraviolet irradiation caused by a diminished ozone absorption capacity in the stratosphere follows a diurnal curve dependent on the elevation of the sun. On the other hand, energy input to the earth's surface through Greenhouse warming takes a less direct route.

Regarding impacts on ozone concentrations and other oxidized species, two distinct types of effects can be seen in the future scenarios; these effects can be linked to the differences in energy input dynamics. Because global surface temperature increases were simulated by the addition of 2 and 5 K to the original, city-specific temperature profiles evenly across the day, the impacts resulting from temperature increases resulted in slight increases in reaction rates, and somewhat greater formation of ozone and oxidized products across the entire simulation period. This is to be expected since most temperature-dependent reaction rates increase with increasing temperature. The second type of impact, resulting from the enhanced (due to depleted stratospheric ozone) ultraviolet irradiation function, was an increase in the rate of photochemical reactivity centered around midday.

In all test cases studied, an increase in photolysis rates due to decreased stratospheric ozone caused a more rapid formation rate for ozone and other oxidized products. Because most additional energy input was concentrated in an already photochemically reactive period of the day, the impact was often more dramatic than that of the temperature change. Levels of ozone at or near the NAAQS (0.12 ppm) were achieved much earlier, sometimes hours earlier, at the time when an air parcel might be over more populated areas earlier in the trajectory. This would occur because the midday enhancement of photolysis rates provides a greater radical production rate and radical concentrations, thereby increasing

short-term reactivity so that these photochemical systems can convert precursors to oxidant more efficiently. However, this enhanced reactivity may not always result in greater maximum ozone concentrations because that measure of oxidant-forming potential is also a function of available precursors and meteorological conditions. Hence, while increased ultraviolet irradiance from depleted stratospheric ozone is predicted to increase short-term reactivity in a urban air parcel, these conditions will not always result in greater maximum concentrations because such long-term measures are more a function of the specific system. Air parcels with low precursor emissions and beneficial meteorological conditions may actually produce lower maximum concentrations of oxidized products because the enhanced reactivity may consume a large fraction of the precursor species under conditions earlier in the day that are less favorable for oxidant formation.

For the general groups of scenarios just described, our simulations predict increases in maximum hourly ozone (over the 0.12 ppm of the future base-case scenarios) at about 1.4 ± 0.5 percent per degree Kelvin increase (2.5 ± 0.9 percent per degree Fahrenheit) for the first three groups, with the Group 1 cities at the more reactive extreme. With respect to changes in ozone column density, we predicted a 1.1 percent increase in maximum hourly ozone concentration for each percent decrease in ozone column for the Group 1 cities, while the rates of increase for the Groups 2 and 3 cities were very near zero. Some of this variability was seen as an artifact of the EKMA calculation procedure (as applied in various SIPs and in our future scenario determinations). That is, since the EKMA procedure terminates its calculations at 1800 hours, additional oxidant-forming potential, which is only realized after 1800 hours, cannot be accounted for. For the Group 1 EKMA attainment and future base-case simulations, 0.12 ppm of ozone was formed at 1800 hours, but there was an increasing slope at that time, indicating additional oxidant-forming potential. Future conditions of enhanced ultraviolet irradiance utilized this potential more efficiently to produce higher levels of ozone prior to 1800 hours. Therefore, those test cases (Group 1) showed more extreme sensitivity to future changes in stratospheric ozone column densities. Such a trend also occurred for the Group 4 days, though for a somewhat different reason. In those tests, a unique set of emission and meteorological variables combined to create a base-case simulation with an apparently large ozone-forming potential, but with fairly low energy input, leading to very little calculated NMOC control to achieve the NAAQS. As the additional energy for the future scenarios was added, however, this system became very reactive and achieved much higher levels of ozone than the base-case simulations. Again, the EKMA procedure, as presently applied, could not be used to account for the overall oxidant-forming potential of this system.

We recognize that simulations in which some of the rates in the chemical mechanism vary between present and future scenarios was never an intended application of the EKMA. On the other hand, when it is possible to account for a large fraction of the oxidant-forming potential, such as in the base-case simulations for Groups 2 and 3 where the ozone maximum concentration occurred prior to 1800 hours, very little additional ozone formation was predicted with changes in future parameters because a large fraction of the oxidant-forming potential was already accounted for. Using our estimates of moderate (+2 K and -16.67 percent ozone column density) and extreme (+5 K and -33.3 percent ozone column density) conditions, we predicted group-average ozone concentrations of 0.132 and 0.120 ppm for Groups 2 and 3 at the extreme conditions. Hence, though ozone forms more rapidly in these future scenarios, the concentrations do not accumulate to much over the NAAQS for even the most extreme conditions tested. Conversely, the Groups 1 and 4 average concentration results were 0.148 and 0.150 ppm for moderate conditions and 0.174 and 0.207 ppm for extreme tests. Because of the rather significant changes predicted for the Group 1 and 4 test cases, we also analyzed the data for an indication of whether synergistic interaction between the two perturbations was predicted to occur. We found that, for the cases available, the combined effects of coincident increases in both parameters were sometimes additive, but not synergistic. Such a finding is consistent with our description of the urban photochemical processes, assuming that there is a limit to the oxidant-forming potential of an air mass.

The formation of other oxidized products such as nitric acid and hydrogen peroxide was found to be specifically dependent on the types of processes by which they form in an urban atmosphere. For instance, the formation rate and eventual yield of nitric acid is related to the hydroxyl radical concentration and the amount of NO_x available. These two parameters are closely linked to ozone concentration, since NO_x is an ozone precursor and ozone photolysis is the key source of hydroxyl radicals in these systems. Hence, the impacts of potential global changes on nitric acid formation parallel those of ozone and are limited by available NO_x . On the other hand, hydrogen peroxide is formed by the combination of hydroperoxy radicals, which only accumulate after NO_x is depleted. An increase in photochemical reactivity will deplete NO_x faster and allow hydroperoxy radical (and therefore, hydrogen peroxide) to form for longer periods and at higher concentrations. In this study, the predicted future increases in photochemical reactivity stem mainly from projected future decreases in ozone column density; thus, hydrogen peroxide was found to be very sensitive to this parameter.

We have also found that NMOC emission control designed to attain the NAAQS for ozone appears to be a very effective hydrogen peroxide control since one net effect of NMOC control is to reduce the reactivity of a system,

thus, to reduce the consumption rate of NO_x . Since hydroperoxy radical concentrations are highly sensitive to NO_x concentration, the additional remaining NO_x holds down the hydrogen peroxide formation rate. Conversely, as projected conditions of future global change were implemented in our test cases, NO_x was again depleted more rapidly and hydrogen peroxide concentrations began to increase significantly. For our moderate test conditions, control of NMOC to attain the ozone NAAQS was predicted to also limit hydrogen peroxide to about 70 to 80 percent of its original base-case concentration. However, as ozone column conditions were changed to the extreme case, more hydrogen peroxide was formed than in the original base case, even with the added NMOC control.

RECOMMENDATIONS

Our experience in both the photolysis rate sensitivity study and the urban photochemical kinetics investigation yields certain recommendations for future study. We have pointed out that the calculation of photolysis rates for ozone [to $\text{O}(^1\text{D})$] and formaldehyde are very critical to atmospheric simulation modeling, and yet are uncertain to unacceptable limits. We feel future efforts to limit this uncertainty would provide additional confidence in all air quality simulation modeling. These efforts should follow two paths: (1) The use of currently existing information to develop improved actinic flux data sets and computer formulations, and (2) additional experimental measurements, particularly of formaldehyde absorption cross sections, short wavelength actinic flux distributions, and actinometrically determined j -values, to provide critical information in the most uncertain areas.

We have established some limits to the extremes of change that could occur in urban scenarios, and suggest that continuation of such an effort should focus on four aspects: (1) Use of the newest and more extensive 1987 SIP data along with the recently developed Carbon-Bond Mechanism-IV/OZIPM-4 model to obtain more specific information related to the extent of the impacts found in this study, (2) use of such models and data to study parameters not varied in this study, but now predicted by GCMs to be variable (including water vapor, mixing height and cloud cover), (3) utilization of regional models such as the ROM or RTM-III, to analyze linked, multiple, urban trajectories in a unified regional domain, and (4), use of a more complex gridded urban model, such as the Urban Airshed Model, in conjunction with demographic data to evaluate the exposure-related impacts of reactivity changes predicted to occur with smaller ozone column densities.

REFERENCES

- Atkinson, R. and A. C. Lloyd. 1984. Evaluation of kinetic and mechanistic data for modeling of photochemical smog. J. Phys. Chem. Ref. Data, 13:315-444.
- Atkinson, R., A. C. Lloyd, and L. Wings. 1982. An updated chemical mechanism for hydrocarbon/ NO_x / SO_2 photooxidations suitable for inclusion in atmospheric simulation models. Atmos. Environ., 16(6):1341-1355.
- Bass, A. M.. 1986. Personal communication.
- Bass, A. M., L. C. Glasgow, C. Miller, J. P. Jesson, and D. L. Filken. 1980. Planet Space Sci., 28:675.
- Bahe, F. C., H. Illner, W. N. Marx, U. Schurath, and P. Roth. 1979a. "Messung der von Veränderungen der Ozonschicht stark abhängigen kurzwelligigen Sonnenstrahlung. Gesellschaft für Strahlen- und Umweltforschung MBH.
- Bahe, F. C., W. N. Marx, U. Schurath, and E. P. Roth. 1979b. Determination of the absolute photolysis rate of ozone by sunlight, $\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\Delta_g)$, at ground level. Atmos. Environ., 13:1515.
- Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson. 1984. Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement II. CODATA task group on gas phase chemical kinetics. J. Phys. Chem. Ref. Data, 13(4):1259-1380.
- Blackburn, T. E. 1984. "Solar Photolysis of Ozone to Singlet D Oxygen Atoms, $\text{O}(^1\text{D})$." Doctoral dissertation, University of Michigan.
- Braslau, N., and J. V. Dave. 1973a. J. Appl. Meteorol., 12:601.
- Braslau, N., and J. V. Dave. 1973b. J. Appl. Meteorol., 12:616.

- Calvert, J. G. 1980. "The Homogeneous Chemistry of Formaldehyde Generation." Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, U.S. Department of Transportation, Washington, DC (May 1980).
- Calvert, J. G., and J. N. Pitts. 1966. Photochemistry, John Wiley, New York.
- Carter, W.P.L., F. W. Lurmann, R. Atkinson, and A. Lloyd. 1986. "Development and Testing of a Surrogate Species Chemical Reaction Mechanism." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (EPA-68-02-4104).
- Cicerone, R. J., S. Walters, and S. C. Liu. 1983. Nonlinear response of stratospheric ozone column to chlorine injections. J. Geophys. Res., 88:3647-3661.
- Craig, H., and C. C. Chou. 1982. Geophys. Res. Lett., 9:1221-1224.
- Dave, J. V. 1972. "Development of Programs for Computing Characteristics of Ultraviolet Radiation." National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland (NASA CR-139134 and NTIS N75-10746/6SL).
- DeLuise, J. J. 1975. J. Geophys. Res., 80:345.
- Demerjian, K. L., K. L. Schere, and J. T. Peterson. 1980. Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower troposphere. Adv. Environ. Sci. Technol., 10:369-460.
- DeMore, W. B., J. J. Margitan, M. J. Molina, R. T. Watson, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara. 1985. "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling." Evaluation Number 7. Jet Propulsion Laboratory, Pasadena, California (85-37).
- Dickinson, R. E., and R. J. Cicerone. 1986. Future global warming from atmospheric trace gases. Nature, 319:109.
- Dickerson, R. R., D. H. Stedman, and A. C. Delany. 1982. Direct measurements of ozone and nitrogen dioxide photolysis rates in the troposphere. J. Geophys. Research, 87(C7):4933-4946.
- Fröhlich, C., and R. W. Brusa. 1981. Solar radiation and its variation in time. Sol. Phys., 74:209-215.

- Gear, C. W. 1971. "The Automatic Integration of Ordinary Differential Equations." In Communication of the Association for Computing Machinery, 14(3):176-179.
- Gery, M. W., G. Z. Whitten, and J. P. Killus. 1988. "Development and Testing of the CBM-IV for Urban and Regional Modeling." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.
- Green, A.E.S., K. R. Cross, and L. A. Smith. 1980. Improved analytic characterization of ultraviolet skylight. Photochem. Photobiol., 31:59-65.
- Hogo, H., and G. Z. Whitten. 1985. "Guidelines for Using OZIPM-3 with CBM-X or Optional Mechanisms. Volume 1. Description of the Ozone Isopleth Plotting Package, Version 3." Systems Applications, Inc., San Rafael, California (SYSAPP-85/191).
- Iqbal, M. 1983. An Introduction to Solar Radiation. Academic Press. Toronto, Canada.
- Jeffries, H. E. 1986. Personal communication.
- Jeffries, H. E., and K. G. Sexton. 1987. "Technical Discussion Related to the Choice of Photolytic Rates for Carbon Bond Mechanisms in OZIPM4/EKMA. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (EPA-450/4-87-003).
- Kerr, R. A. 1987. Has stratospheric ozone started to disappear? Science, 237:131-132.
- Lurmann, F. W., W.P.L. Carter, and L. A. Coyner. 1987. "A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models. Volume II. Guidelines for Using the Mechanism."
- Moortgat, G. K. 1986. Personal communication.
- Moortgat, G. K., F. Slemr, W. Seiler, and P. Warneck. 1978. Photolysis of formaldehyde: Relative quantum yields of H_2 and CO in the wavelengthrange 270-360 nm. Chem. Phys. Lett., 54(3):444.
- Moortgat, G. K., and P. Warneck. 1979. CO and H_2 quantum yields in the photodecomposition of formaldehyde in air. J. Chem. Phys., 70(8):3639.

- Peterson, J. T. 1977. Dependence of the NO_2 photodissociation rate constant on altitude. Atmos. Environ., 11:689-695.
- Prather, M. J., M. B. McElroy, and S. C. Wofsy. 1984. Reductions in ozone at high concentrations of stratospheric halogens. Nature, 312:227-231.
- Ramanathan, V., R. J. Cicerone, H. B. Singh, and J. T. Kiehl. 1985. Trace gas trends and their potential role in climate change. J. Geophys. Res., 90:5547-5566.
- Schere, K. 1986. Personal communication.
- Schippnick, P. F., and A.E.S. Green. 1982. Analytical characterization of spectral actinic flux and spectral irradiance in the middle ultraviolet. Photochemistry and Photobiology, 35:89-101.
- Wang, W. C., D. J. Wuebbles, W. M. Washington, R. G. Isaacs, and G. Molnar. 1986. Trace gases and other potential perturbations to global climate. Rev. of Geophysics, 24:110-140.
- Weiss, R. F. 1981. J. Geophys. Res., 86:7185-7195.
- Whitten, G. Z. 1983. The chemistry of smog formation: A review of current knowledge. Environ. Int., 9:447-463.
- Whitten, G. Z., and H. Hogo. 1980. "Volume II. CHEMK: A Computer Modeling Scheme for Chemical Kinetics." Systems Applications, Inc., San Rafael, California (EPA-600/3-80-028b).
- Whitten, G. Z., J. P. Killus, and R. G. Johnson. 1985. "Modeling of Auto Exhaust Smog Chamber Data for EKMA Development." Systems Applications, Inc., San Rafael, California (EPA-600/3-85-025).
- WMO. 1985. Atmospheric Ozone 1985. Assessment of Our Understanding of the Processes Controlling Its Present Distribution and Change. World Meteorological Organization, Geneva, Switzerland.

Appendix A

INPUT DATA USED FOR THE OZIPM/EKMA SIMULATIONS

The values in this appendix were used as input for the OZIPM/EKMA simulations described in the text. As noted in the text, the temperature values shown were used in the base case simulations. These values were incremented by 2 K and 5 K for the future sensitivity simulations.

BOSTON

Elevation = 5 m
Regional Albedo = 0.14

Longitude = 71.1 W
Latitude = 42.3 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
053078	293.1	294.2	295.1	295.8	296.3	296.6	296.6	296.3	295.8	295.1	294.1
072178	298.4	299.4	300.1	300.6	300.7	300.6	300.1	299.4	298.4	297.2	295.9
081378	292.5	293.3	294.0	294.6	295.0	295.3	295.3	295.2	294.9	294.4	293.7
081578	295.0	295.6	296.1	296.4	296.7	296.8	296.8	296.6	296.3	295.9	295.5
081678	297.1	297.6	298.0	298.2	298.4	298.5	298.5	298.5	298.4	298.2	298.0
062979	291.4	293.0	294.4	295.5	296.3	296.7	296.7	296.4	295.7	294.7	293.3
071079	294.0	294.1	294.1	294.0	293.8	293.5	293.2	292.8	292.4	292.0	291.6

Mixing Height (m) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
053078	250.0	305.7	359.8	410.5	456.3	495.9	528.0	551.6	566.1	571.0	566.1
072178	250.0	568.2	874.2	1156.1	1403.3	1606.1	1756.8	1849.7	1881.0	1849.7	1756.8
081378	250.0	293.6	335.0	372.2	403.2	426.6	441.1	446.0	441.1	426.6	403.2
081578	250.0	331.4	408.8	478.2	536.2	579.8	606.8	616.0	606.8	579.8	536.2
081678	250.0	485.3	704.5	892.8	1037.2	1128.0	1159.0	1128.0	1037.2	892.8	704.5
062979	449.0	532.1	612.0	685.7	750.2	803.2	842.6	866.8	875.0	866.8	842.6
071079	360.0	692.0	1007.4	1290.2	1526.5	1704.2	1814.6	1852.0	1814.6	1704.2	1526.5

CHICAGO

Elevation = 185 m
Regional Albedo = 0.14

Longitude = 87.7 W
Latitude = 41.8 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
071079	294.9	295.2	295.2	295.1	294.8	294.3	293.7	293.0	292.2	291.3	290.4
071179	296.3	297.2	297.9	298.5	298.8	298.9	298.8	298.4	297.8	297.1	296.2
082680	297.6	298.3	298.9	299.2	299.3	299.1	298.7	298.0	297.2	296.2	295.1

167

Mixing Height (m) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
071079	250.0	606.4	949.2	1265.0	1541.9	1769.1	1937.9	2041.9	2077.0	2041.9	1937.9
071179	250.0	383.1	511.0	628.9	732.2	817.1	880.1	918.9	932.0	918.9	880.1
082680	250.0	533.9	806.8	1058.4	1278.8	1459.8	1594.2	1677.0	1705.0	1677.0	1594.2

LOS ANGELES

Elevation = 0 m
Regional Albedo = 0.14

Longitude = 118.33 W
Latitude = 34.1 N

Temperature (K) Profiles:

Hours from Start		Temperature (K)									
Temperature (K)											
DATE	0	1	2	3	4	5	6	7	8	9	10
062674	307.8	307.3	304.7	303.8	300.5	303.3	300.3	298.3	296.9	296.5	296.1
	11	12	13	14	15	16	17	18	19	20	21
	295.7	295.3	294.9	296.4	298.8	301.9	304.8	307.9	310.1	311.7	314.0
	22	23	24								
	315.5	316.6	314.6								

Mixing Height (m) Profiles:

Hours from Start		Mixing Height (m)									
Temperature (K)											
DATE	0	1	2	3	4	5	6	7	8	9	10
062674	335.8	314.2	267.7	212.3	176.6	137.2	137.9	107.8	103.0	94.8	90.2
	11	12	13	14	15	16	17	18	19	20	21
	85.4	80.0	73.9	72.2	79.3	70.1	116.2	156.3	300.7	356.9	447.5
	22	23	24								
	528.4	539.1	523.9								

NASHVILLE

Elevation = 180 m
Regional Albedo = 0.14

Longitude = 86.8 W
Latitude = 36.2 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
070280	298.3	300.1	301.7	303.0	304.0	304.5	304.7	304.5	303.9	302.9	301.5
072580*	298.3	300.2	301.9	303.3	304.3	304.9	305.1	304.9	304.3	303.3	301.9
080180*	299.6	301.2	302.5	303.6	304.5	305.0	305.1	305.0	304.5	303.6	302.5
081080*	299.8	301.8	303.6	305.1	306.1	306.7	306.8	306.4	305.6	304.4	302.8
091181	291.0	293.8	296.3	298.3	299.8	300.8	301.1	300.8	299.8	298.3	296.2
091281	293.1	295.7	298.0	299.8	301.2	302.1	302.4	302.1	301.2	299.8	298.0

Mixing Height (m) Profiles: (DILU option used)

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
070280	250.0	530.5	881.9	1209.7	1451.4	1622.0	1747.3	1845.0	1845.0	1845.0	1845.0
072580*	250.0	546.6	908.6	1233.5	1466.6	1629.8	1750.3	1845.0	1845.0	1845.0	1845.0
080180*	250.0	542.0	904.9	1232.7	1467.1	1630.4	1750.7	1845.0	1845.0	1845.0	1845.0
081080*	250.0	527.5	889.2	1224.0	1463.8	1629.6	1750.5	1845.0	1845.0	1845.0	1845.0
091181	250.0	516.9	892.4	1238.3	1477.0	1637.3	1753.3	1845.0	1845.0	1845.0	1845.0
091281	250.0	503.1	874.5	1226.0	1470.9	1634.8	1752.5	1845.0	1845.0	1845.0	1845.0

* Multiple trajectories for this date had identical profiles

NEW YORK

Elevation = 2 m
Regional Albedo = 0.14

Longitude = 73.9 W
Latitude = 40.8 N

Temperature (K) Profiles:

<u>Hours from Start</u>											
<u>DATE</u>	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
062480*	296.9	297.3	297.6	297.7	297.7	297.5	297.2	296.8	296.4	295.9	295.3

Mixing Height (m) Profiles:

<u>Hours from Start</u>											
<u>DATE</u>	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
062480*	300.0	611.5	907.4	1172.9	1394.6	1561.4	1664.9	1700.0	1664.9	1561.4	1394.6

* Multiple trajectories for this date had identical profiles

PHILADELPHIA

Elevation = 2 m
Regional Albedo = 0.14

Longitude = 75.2 W
Latitude = 40.0 N

Temperature (K) Profiles:

Hours from Start											
DATE	0	1	2	3	4	5	6	7	8	9	10
071379	298.7	299.8	300.6	301.2	301.6	301.8	301.6	301.3	300.7	299.9	299.0
071979	295.8	296.2	296.5	296.8	296.9	297.0	297.0	297.0	296.9	296.8	296.5
062480	298.7	299.8	300.6	301.2	301.6	301.8	301.6	301.3	300.7	299.9	299.0
061581	292.9	293.9	294.6	295.0	295.2	295.0	294.5	293.7	292.6	291.3	289.8
061681	297.9	298.8	299.5	300.0	300.2	300.3	300.1	299.8	299.3	298.6	297.7
081982	293.9	294.5	294.8	295.0	295.0	294.8	294.5	294.0	293.5	292.9	292.2
062783*	296.1	297.1	297.9	298.6	299.0	299.1	299.0	298.7	298.2	297.5	296.5

Mixing Height (m) Profiles:

Hours from Start											
DATE	0	1	2	3	4	5	6	7	8	9	10
071379	250.0	468.5	676.1	862.3	1017.8	1134.8	1207.4	1232.0	1207.4	1134.8	1017.8
071979	250.0	478.3	691.0	873.7	1013.8	1101.9	1132.0	1101.9	1013.8	873.7	691.0
062480	250.0	413.6	619.2	811.8	954.3	1055.0	1129.0	1186.0	1235.0	1235.0	1235.0
061581	250.0	476.8	698.1	908.3	1102.3	1275.3	1423.1	1542.0	1629.0	1682.1	1700.0
061681	250.0	487.4	713.0	915.3	1084.2	1211.3	1290.2	1317.0	1290.2	1211.3	1084.2
081982	250.0	598.0	928.6	1225.1	1472.8	1659.1	1774.8	1814.0	1774.8	1659.1	1472.8
062783*	250.0	434.2	609.3	766.2	897.4	966.0	1057.2	1078.0	1057.2	996.0	897.4

* Multiple trajectories for this date had identical profiles

PHOENIX

Elevation = 340 m
Regional Albedo = 0.28

Longitude = 112.0 W
Latitude = 33.4 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
070584	306.5	307.1	307.5	307.7	307.6	307.2	306.6	305.7	304.5	303.2	301.8
082984	307.2	306.9	306.4	305.7	304.8	303.7	302.5	301.1	299.7	298.3	297.0
083184	307.8	306.7	305.5	304.2	302.9	301.5	300.2	299.0	297.9	296.9	296.1
091484*	305.2	305.7	306.0	306.1	305.8	305.3	304.5	303.5	302.3	300.9	299.4

Mixing Height (m) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
070584	530.0	730.0	1000.0	1200.0	1400.0	1600.0	1800.0	2000.0	2200.0	2400.0	2400.0
082984	250.0	300.0	600.0	944.0	1488.0	2032.0	2576.0	2938.0	3119.0	3300.0	3300.0
083184	250.0	300.0	350.0	600.0	1050.0	1650.0	2250.0	2750.0	3050.0	3300.0	3300.0
091484*	250.0	300.0	350.0	850.0	1350.0	1850.0	2000.0	2150.0	2300.0	2400.0	2400.0

* Multiple trajectories for this date had identical profiles

SEATTLE

Elevation = 122 m
Regional Albedo = 0.14

Longitude = 122.3 W
Latitude = 47.6 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
080781*	296.7	298.4	300.0	301.2	302.0	302.5	302.6	302.3	301.6	300.6	299.3
081081*	297.8	300.3	302.4	304.1	305.3	306.1	306.2	305.8	304.9	303.5	301.6
081181*	297.8	300.1	302.0	303.6	304.7	305.3	305.4	304.9	304.0	302.7	300.9

Mixing Height (m) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
080781*	250.0	343.7	432.7	512.5	579.2	629.3	660.4	671.0	660.4	629.3	579.2
081081*	250.0	357.3	459.1	550.5	626.8	684.3	719.9	732.0	719.9	684.3	626.8
081181*	250.0	397.8	538.1	664.0	769.1	848.2	897.4	914.0	897.4	848.2	769.1

* Multiple trajectories for this date had identical profiles

TULSA

Elevation = 198 m
Regional Albedo = 0.18

Longitude = 96.0 W
Latitude = 36.2 N

Temperature (K) Profiles:

Hours from Start		Temperature (K) Profiles:									
DATE	0	1	2	3	4	5	6	7	8	9	10
070181	298.4	298.9	299.3	299.4	299.4	299.1	298.6	297.9	297.0	296.0	294.8
071681*	300.8	301.5	301.9	302.1	302.0	301.6	301.0	300.0	298.8	297.5	296.0
080681	302.0	302.3	302.5	302.5	302.3	301.9	301.3	300.5	299.5	298.4	297.2
062982	296.9	297.8	298.5	298.9	299.0	298.8	298.2	297.4	296.3	294.9	293.4
080682	301.2	301.5	301.6	301.5	301.3	300.8	300.2	299.4	298.4	297.4	296.2
082382	299.3	299.7	299.9	299.7	299.2	298.5	297.4	296.0	294.4	292.7	290.8
072683	301.4	302.3	302.8	303.1	303.0	302.6	301.9	300.9	299.6	298.0	296.3
082783	299.9	299.5	299.0	298.3	297.4	296.4	295.3	294.1	292.8	291.6	290.4
082883	299.1	298.5	297.9	297.1	296.2	295.2	294.2	293.1	292.1	291.1	290.1

Mixing Height (m) Profiles:

Hours from Start		Mixing Height (m) Profiles:									
DATE	0	1	2	3	4	5	6	7	8	9	10
070181	250.0	500.6	743.5	971.5	1177.5	1355.4	1499.7	1606.0	1671.1	1693.0	1671.1
071681*	250.0	586.7	913.2	1219.5	1496.4	1735.4	1929.2	2072.1	2159.5	2189.0	2159.5
080681	250.0	550.4	841.7	1115.0	1362.0	1575.3	1748.2	1875.7	1953.7	1980.0	1953.7
062982	250.0	538.8	818.8	1081.5	1319.0	1523.9	1690.2	1812.7	1887.7	1913.0	1887.7
080682	250.0	550.4	841.7	1115.0	1362.0	1575.3	1748.2	1875.7	1953.7	1980.0	1953.7
082382	250.0	760.0	1254.5	1718.5	2137.9	2499.9	2793.5	3009.9	3142.4	3187.0	3142.4
072683	250.0	616.2	971.3	1304.5	1605.6	1865.6	2076.4	2231.8	2327.0	2359.0	2327.0
082783	250.0	732.0	1199.4	1638.0	2034.4	2376.5	2654.1	2858.6	2983.8	3026.0	2983.8
082883	250.0	684.5	1105.7	1501.0	1858.3	2166.6	2416.8	2601.1	2714.0	2752.0	2714.0

* Multiple trajectories for this date had identical profiles

WASHINGTON

Elevation = 4 m
Regional Albedo = 0.14

Longitude = 77.1 W
Latitude = 38.9 N

Temperature (K) Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
071680	300.9	301.5	301.9	302.0	301.8	301.4	300.6	299.5	298.1	296.5	294.7
071780	300.9	301.5	301.9	302.0	301.8	301.4	300.6	299.5	298.1	296.5	294.7
072180	300.9	301.5	301.9	302.0	301.8	301.4	300.6	299.5	298.1	296.5	294.7
080780	299.5	300.5	301.2	301.7	302.0	301.9	301.4	300.7	299.6	298.3	296.7
082980	301.0	301.5	301.8	301.8	301.6	301.0	300.2	299.1	297.6	296.0	294.1

Mixing Height Profiles:

Hours from Start

DATE	0	1	2	3	4	5	6	7	8	9	10
071680	160.0	438.0	711.3	975.1	1225.0	1456.7	1666.1	1849.8	2004.6	2127.9	2217.4
071780	160.0	438.0	711.3	975.1	1225.0	1456.7	1666.1	1849.8	2004.6	2127.9	2217.4
072180	160.0	438.0	711.3	975.1	1225.0	1456.7	1666.1	1849.8	2004.6	2127.9	2217.4
080780	420.0	594.9	766.8	932.8	1090.0	1235.7	1367.5	1483.1	1580.5	1658.0	1714.3
082980	150.0	443.7	732.3	1011.0	1275.0	1519.7	1741.0	1935.0	2098.6	2228.7	2323.3

Appendix B

PHOTOLYSIS RATE RATIOS AS A FUNCTION OF ZENITH ANGLE FOR A NUMBER OF TEST CITIES

This appendix contains photolysis rate ratios (to j_{NO_2}) as a function of zenith angle for a number of test cities. These values differ for each city only in regard to regional albedo and elevation. Because elevation and albedo are very similar for our set of test cities, only minor variations are evident. The values were compiled using the formulation of Schippnick and Green (1982) and the extraterrestrial flux data of WRC (Iqbal, 1988) for three different ozone column densities. The rate ratios for 0.300 cm-atm (300 Dobson Units) were used in the base-case simulations; 0.250 and 0.200 cm-atm values were employed in future scenario simulations.

Table B-1. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Boston, MA.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.084	3.428	4.234	0.746	1.151
10	3.976	3.399	4.218	0.735	1.143
20	3.658	3.312	4.170	0.702	1.120
30	3.154	3.161	4.085	0.646	1.081
40	2.505	2.941	3.954	0.569	1.024
50	1.774	2.642	3.763	0.471	0.946
60	1.056	2.250	3.486	0.357	0.842
70	0.482	1.756	3.081	0.234	0.708
78	0.215	1.302	2.638	0.145	0.580
86	0.094	0.802	2.039	0.074	0.427
0.250 cm-atm:					
0	5.415	3.706	4.344	0.869	1.220
10	5.279	3.676	4.329	0.856	1.213
20	4.879	3.585	4.281	0.819	1.188
30	4.243	3.429	4.195	0.757	1.147
40	3.417	3.200	4.065	0.670	1.087
50	2.476	2.887	3.875	0.560	1.005
60	1.529	2.474	3.598	0.430	0.896
70	0.739	1.951	3.191	0.288	0.754
78	0.343	1.462	2.741	0.182	0.617
86	0.147	0.904	2.121	0.093	0.452
0.200 cm-atm:					
0	7.483	4.050	4.472	1.036	1.309
10	7.305	4.019	4.457	1.021	1.301
20	6.784	3.924	4.409	0.979	1.275
30	5.951	3.761	4.324	0.909	1.231
40	4.862	3.522	4.194	0.810	1.167
50	3.606	3.193	4.004	0.683	1.080
60	2.317	2.757	3.727	0.532	0.964
70	1.192	2.197	3.318	0.365	0.812
78	0.582	1.666	2.861	0.236	0.665
86	0.245	1.034	2.215	0.121	0.484

Table B-2. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Chicago, IL.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.131	3.459	4.266	0.753	1.160
10	4.021	3.430	4.250	0.742	1.153
20	3.702	3.342	4.202	0.709	1.130
30	3.194	3.192	4.118	0.653	1.091
40	2.540	2.973	3.988	0.576	1.034
50	1.803	2.674	3.799	0.478	0.956
60	1.077	2.281	3.523	0.362	0.852
70	0.494	1.783	3.116	0.239	0.717
78	0.222	1.323	2.664	0.149	0.586
86	0.099	0.826	2.073	0.077	0.435
0.250 cm-atm:					
0	5.482	3.741	4.378	0.878	1.231
10	5.345	3.711	4.363	0.866	1.223
20	4.943	3.621	4.315	0.828	1.199
30	4.301	3.465	4.231	0.766	1.158
40	3.469	3.236	4.102	0.679	1.098
50	2.518	2.923	3.913	0.569	1.016
60	1.561	2.510	3.637	0.437	0.907
70	0.759	1.982	3.228	0.294	0.764
78	0.356	1.486	2.769	0.187	0.625
86	0.156	0.931	2.156	0.097	0.461
0.200 cm-atm:					
0	7.586	4.091	4.509	1.048	1.322
10	7.406	4.061	4.494	1.034	1.313
20	6.881	3.966	4.447	0.991	1.288
30	6.041	3.804	4.363	0.920	1.244
40	4.942	3.565	4.234	0.821	1.180
50	3.673	3.236	4.046	0.694	1.092
60	2.367	2.799	3.769	0.542	0.976
70	1.225	2.234	3.357	0.373	0.824
78	0.603	1.694	2.891	0.242	0.674
86	0.259	1.065	2.252	0.126	0.494

Table B-3. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Los Angeles, CA.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.105	3.442	4.248	0.749	1.155
10	3.996	3.413	4.233	0.738	1.147
20	3.677	3.325	4.184	0.705	1.125
30	3.171	3.175	4.099	0.649	1.086
40	2.520	2.955	3.969	0.572	1.028
50	1.787	2.656	3.779	0.474	0.950
60	1.065	2.264	3.502	0.359	0.847
70	0.487	1.768	3.097	0.236	0.712
78	0.218	1.311	2.649	0.147	0.583
86	0.096	0.813	2.055	0.076	0.431
0.250 cm-atm:					
0	5.444	3.721	4.359	0.873	1.225
10	5.308	3.691	4.344	0.860	1.217
20	4.907	3.601	4.296	0.823	1.193
30	4.268	3.445	4.211	0.761	1.152
40	3.440	3.216	4.082	0.674	1.092
50	2.495	2.903	3.892	0.564	1.010
60	1.544	2.490	3.615	0.433	0.901
70	0.748	1.965	3.208	0.291	0.759
78	0.349	1.473	2.754	0.184	0.621
86	0.151	0.917	2.137	0.095	0.456
0.200 cm-atm:					
0	7.528	4.068	4.489	1.041	1.315
10	7.350	4.037	4.473	1.027	1.306
20	6.826	3.943	4.426	0.984	1.281
30	5.991	3.780	4.341	0.914	1.237
40	4.898	3.541	4.212	0.815	1.173
50	3.636	3.212	4.022	0.688	1.085
60	2.339	2.775	3.746	0.536	0.969
70	1.207	2.213	3.336	0.369	0.817
78	0.591	1.679	2.874	0.239	0.669
86	0.251	1.048	2.232	0.123	0.488

Table B-4. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Nashville, TN.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.130	3.458	4.265	0.753	1.160
10	4.020	3.429	4.249	0.742	1.152
20	3.701	3.342	4.201	0.709	1.130
30	3.193	3.192	4.117	0.653	1.091
40	2.539	2.972	3.987	0.575	1.034
50	1.802	2.673	3.798	0.477	0.956
60	1.076	2.280	3.522	0.362	0.852
70	0.494	1.783	3.115	0.239	0.717
78	0.222	1.322	2.663	0.149	0.586
86	0.099	0.826	2.072	0.077	0.435
0.250 cm-atm:					
0	5.480	3.740	4.377	0.878	1.231
10	5.343	3.710	4.362	0.865	1.223
20	4.941	3.620	4.314	0.828	1.199
30	4.300	3.464	4.230	0.766	1.158
40	3.467	3.235	4.101	0.679	1.098
50	2.517	2.922	3.912	0.583	1.016
60	1.560	2.509	3.636	0.437	0.906
70	0.759	1.981	3.227	0.294	0.764
78	3.552	1.486	2.768	0.187	0.625
86	0.155	0.931	2.155	0.097	0.461
0.200 cm-atm:					
0	7.583	4.090	4.508	1.047	1.321
10	7.404	4.060	4.493	1.033	1.313
20	6.879	3.965	4.446	0.991	1.287
30	6.038	3.803	4.362	0.920	1.244
40	4.940	3.564	4.233	0.821	1.180
50	3.672	3.235	4.044	0.694	1.092
60	2.366	2.798	3.768	0.542	0.976
70	1.225	2.233	3.356	0.373	0.823
78	0.602	1.694	2.890	0.242	0.673
86	0.259	1.064	2.251	0.126	0.493

Table B-5. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for New York, NY.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.084	3.428	4.234	0.746	1.151
10	3.975	3.399	4.218	0.735	1.143
20	3.658	3.312	4.170	0.702	1.120
30	3.153	3.161	4.084	0.646	1.081
40	2.504	2.941	3.954	0.569	1.024
50	1.774	2.642	3.762	0.471	0.946
60	1.056	2.250	3.486	0.356	0.842
70	0.482	1.756	3.081	0.234	0.708
78	0.215	1.301	2.637	0.145	0.580
86	0.094	0.802	2.039	0.074	0.427
0.250 cm-atm:					
0	5.415	3.705	4.344	0.869	1.220
10	5.278	3.676	4.328	0.856	1.212
20	4.878	3.585	4.280	0.819	1.188
30	4.242	3.429	4.195	0.757	1.147
40	3.417	3.199	4.065	0.670	1.087
50	2.475	2.886	3.874	0.560	1.005
60	1.529	2.474	3.597	0.430	0.896
70	0.739	1.950	3.191	0.288	0.754
78	0.343	1.462	2.741	0.182	0.617
86	0.147	0.904	2.120	0.093	0.452
0.200 cm-atm:					
0	7.482	4.049	4.472	1.035	1.309
10	7.305	4.018	4.457	1.021	1.301
20	6.783	3.923	4.408	0.979	1.275
30	5.949	3.761	4.324	0.908	1.231
40	4.861	3.522	4.194	0.810	1.167
50	3.606	3.192	4.004	0.683	1.079
60	2.316	2.756	3.726	0.532	0.963
70	1.192	2.196	3.318	0.365	0.812
78	0.581	1.665	2.861	0.236	0.665
86	0.245	1.034	2.214	0.121	0.484

Table B-6. Photolysis Rate Ratios to k_{NO_2} (x 1000) for Philadelphia, PA.

Zenith Angle (deg.)	j-values (min^{-1} , x 1000)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.083	3.428	4.234	0.746	1.151
10	3.975	3.399	4.218	0.735	1.143
20	3.657	3.311	4.169	0.701	1.120
30	3.153	3.161	4.084	0.646	1.081
40	2.504	2.941	3.953	0.569	1.024
50	1.773	2.641	3.762	0.471	0.946
60	1.056	2.250	3.486	0.356	0.842
70	0.481	1.755	3.081	0.234	0.708
78	0.215	1.301	2.637	0.145	0.579
86	0.094	0.802	2.039	0.074	0.427
0.250 cm-atm:					
0	5.414	3.705	4.344	0.869	1.220
10	5.278	3.676	4.328	0.856	1.212
20	4.878	3.584	4.280	0.819	1.188
30	4.242	3.428	4.195	0.757	1.147
40	3.416	3.199	4.065	0.670	1.087
50	2.475	2.886	3.874	0.560	1.005
60	1.529	2.474	3.597	0.430	0.896
70	0.739	1.950	3.191	0.288	0.754
78	0.343	1.461	2.741	0.182	0.617
86	0.147	0.904	2.120	0.093	0.452
0.200 cm-atm:					
0	7.481	4.049	4.472	1.035	1.309
10	7.304	4.018	4.456	1.021	1.301
20	6.783	3.923	4.408	0.979	1.275
30	5.949	3.760	4.323	0.908	1.231
40	4.860	3.521	4.194	0.809	1.167
50	3.605	3.192	4.003	0.683	1.079
60	2.316	2.756	3.726	0.532	0.963
70	1.192	2.196	3.317	0.365	0.812
78	0.581	1.665	2.860	0.236	0.665
86	0.244	1.034	2.214	0.121	0.484

Table B-7. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Phoenix, AZ.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.150	3.450	4.254	0.753	1.158
10	4.041	3.421	4.238	0.742	1.150
20	3.720	3.333	4.190	0.708	1.127
30	3.211	3.183	4.106	0.652	1.088
40	2.554	2.963	3.975	0.575	1.031
50	1.812	2.664	3.786	0.477	0.953
60	1.082	2.273	3.512	0.362	0.850
70	0.497	1.780	3.110	0.239	0.716
78	0.225	1.326	2.665	0.150	0.587
86	0.103	0.842	2.096	0.079	0.441
0.250 cm-atm:					
0	5.511	3.732	4.366	0.878	1.228
10	5.374	3.702	4.351	0.865	1.220
20	4.969	3.611	4.303	0.828	1.196
30	4.325	3.455	4.219	0.765	1.155
40	3.488	3.225	4.089	0.678	1.095
50	2.532	2.912	3.900	0.568	1.013
60	1.569	2.501	3.625	0.436	0.904
70	0.764	1.979	3.222	0.294	0.763
78	0.360	1.490	2.771	0.188	0.626
86	0.161	0.949	2.180	0.010	0.467
0.200 cm-atm:					
0	7.630	4.082	4.497	1.048	1.319
10	7.450	4.050	4.481	1.034	1.310
20	6.922	3.955	4.433	0.991	1.285
30	6.075	3.793	4.349	0.920	1.241
40	4.969	3.553	4.220	0.820	1.176
50	3.692	3.224	4.032	0.693	1.089
60	2.378	2.789	3.757	0.541	0.973
70	1.232	2.230	3.351	0.373	0.822
78	0.610	1.699	2.893	0.243	0.675
86	0.268	1.086	2.277	0.129	0.500

Table B-8. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Seattle, WA.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \rightarrow \text{rads}$</u>	<u>$\text{HCHO} \rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.115	3.448	4.255	0.751	1.157
10	4.006	3.420	4.240	0.740	1.150
20	3.687	3.332	4.191	0.706	1.127
30	3.180	3.182	4.107	0.651	1.088
40	2.528	2.963	3.977	0.573	1.031
50	1.793	2.663	3.787	0.475	0.952
60	1.070	2.271	3.511	0.360	0.849
70	0.490	1.774	3.104	0.237	0.714
78	0.220	1.316	2.655	0.148	0.584
86	0.098	0.818	2.062	0.076	0.432
0.250 cm-atm:					
0	5.459	3.729	4.367	0.875	1.227
10	5.322	3.699	4.351	0.862	1.220
20	4.921	3.609	4.304	0.825	1.196
30	4.282	3.453	4.219	0.763	1.154
40	3.451	3.224	4.090	0.676	1.094
50	2.504	2.911	3.900	0.566	1.012
60	1.550	2.498	3.624	0.435	0.903
70	0.752	1.972	3.216	0.292	0.761
78	0.352	1.478	2.760	0.185	0.622
86	0.153	0.922	2.145	0.096	0.458
0.200 cm-atm:					
0	7.551	4.077	4.497	1.044	1.318
10	7.372	4.046	4.814	1.029	1.309
20	6.848	3.952	4.434	0.987	1.283
30	6.010	3.790	4.350	0.916	1.240
40	4.915	3.551	4.221	0.817	1.176
50	3.651	3.222	4.032	0.690	1.088
60	2.350	2.785	3.755	0.539	0.972
70	1.214	2.221	3.344	0.370	0.820
78	0.596	1.685	2.881	0.240	0.671
86	0.254	1.055	2.240	0.124	0.490

Table B-9. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Tulsa, OK.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	<u>$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$</u>	<u>$\text{HCHO} \Rightarrow \text{rads}$</u>	<u>$\text{HCHO} \Rightarrow \text{stab}$</u>	<u>ALD2</u>	<u>H_2O_2</u>
0.300 cm-atm:					
0	4.130	3.450	4.256	0.752	1.158
10	4.021	3.422	4.241	0.741	1.150
20	3.701	3.334	4.192	0.707	1.127
30	3.193	3.184	4.108	0.652	1.088
40	2.539	2.964	3.978	0.574	1.031
50	1.801	2.665	3.789	0.476	0.953
60	1.075	2.273	3.513	0.361	0.850
70	0.493	1.778	3.109	0.238	0.715
78	0.222	1.321	2.660	0.149	0.585
86	0.010	0.827	2.075	0.077	0.435
0.250 cm-atm:					
0	5.485	3.733	4.370	0.877	1.229
10	5.347	3.703	4.354	0.864	1.221
20	4.945	3.613	4.307	0.827	1.197
30	4.303	3.457	4.222	0.765	1.156
40	3.469	3.228	4.093	0.678	1.096
50	2.518	2.916	3.904	0.567	1.013
60	1.560	2.504	3.629	0.436	0.905
70	0.758	1.978	3.222	0.294	0.763
78	0.356	1.485	2.767	0.187	0.624
86	0.156	0.934	2.160	0.098	0.462
0.200 cm-atm:					
0	7.589	4.083	4.500	1.046	1.319
10	7.410	4.052	4.485	1.032	1.311
20	6.884	3.958	4.438	0.990	1.285
30	6.042	3.795	4.354	0.919	1.241
40	4.942	3.556	4.225	0.820	1.177
50	3.672	3.227	4.036	0.693	1.090
60	2.365	2.791	3.761	0.540	0.974
70	1.224	2.229	3.351	0.372	0.822
78	0.603	1.693	2.888	0.242	0.673
86	0.260	1.068	2.256	0.127	0.495

Table B-10. Photolysis Rate Ratios to k_{NO_2} ($\times 1000$) for Washington, DC.

Zenith Angle (deg.)	j-values (min^{-1} , $\times 1000$)				
	$\text{O}_3 \Rightarrow \text{O}(^1\text{D})$	$\text{HCHO} \Rightarrow \text{rads}$	$\text{HCHO} \Rightarrow \text{stab}$	ALD2	H_2O_2
0.300 cm-atm:					
0	4.084	3.428	4.234	0.746	1.151
10	3.976	3.399	4.218	0.735	1.143
20	3.657	3.312	4.170	0.701	1.120
30	3.154	3.161	4.084	0.646	1.081
40	2.504	2.941	3.954	0.569	1.024
50	1.774	2.642	3.763	0.471	0.946
60	1.056	2.250	3.486	0.357	0.842
70	0.482	1.756	3.081	0.234	0.708
78	0.215	1.301	2.637	0.145	0.580
86	0.094	0.802	2.039	0.074	0.427
0.250 cm-atm:					
0	5.414	3.705	4.344	0.869	1.220
10	5.278	3.675	4.328	0.856	1.212
20	4.879	3.585	4.280	0.819	1.188
30	4.242	3.429	4.195	0.757	1.147
40	3.417	3.200	4.065	0.670	1.087
50	2.476	2.886	3.874	0.560	1.005
60	1.529	2.474	3.598	0.430	0.896
70	0.739	1.950	3.191	0.288	0.754
78	0.343	1.462	2.741	0.182	0.617
86	0.147	0.904	2.120	0.093	0.452
0.200 cm-atm:					
0	7.482	4.049	4.472	1.036	1.309
10	7.305	4.019	4.457	1.021	1.301
20	6.783	3.924	4.409	0.979	1.275
30	5.950	3.761	4.324	0.909	1.231
40	4.862	3.522	4.194	0.810	1.167
50	3.606	3.193	4.004	0.683	1.079
60	2.316	2.756	3.727	0.532	0.963
70	1.192	2.196	3.318	0.365	0.812
78	0.582	1.666	2.861	0.236	0.665
86	0.245	1.034	2.214	0.121	0.484